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(54) Title: DIGITAL INFORMATION RECORDING MEDIA AND METHOD OF USING SAME

(57) Abstract

A digital information recording media which includes a recording layer comprising a light-stable colored composition which composition is mutable or decolorizable upon exposure to a specific wavelength of ultraviolet radiation. The light-stable colored composition includes a colorant and an ultraviolet radiation transorber. The colorant, in the presence of the radiation transorber, is adapted, upon exposure of the transorber to specific, narrow bandwidth ultraviolet radiation, to be mutable. The radiation transorber also imparts light-stability to the colorant so that the colorant does not fade when exposed to sunlight or artificial light. The ultraviolet radiation transorber is adapted to absorb radiation and interact with the colorant to effect the irreversible mutation of the colorant. Especially useful radiation is incoherent, pulsed ultraviolet radiation produced by a dielectric barrier discharge excimer lamp or coherent, pulse radiation produced by an excimer laser. In another embodiment, the colored composition which comprises a colorant and an ultraviolet radiation transorber may also contain a molecular includant having a chemical structure which defines at least one cavity. Each of the colorant and radiation transorber is associated with the molecular includant. In some embodiments, the colorant is at least partially included within a cavity of the molecular includant and the ultraviolet radiation transorber is associated with the molecular includant outside of the cavity. In other embodiments, the radiation transorber is covalently coupled to the molecular includant.

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DIGITAL INFORMATION RECORDING MEDIA AND METHOD OF USING SAME

Technical Field

The present invention relates to digital information recording media, such as optical disks. The present invention more particularly relates to digital information recording media which includes a recording layer comprising a mutable dye which layer is mutable or erasable upon exposure to a specific wavelength of ultraviolet radiation, but is color-stable in sunlight or artificial light. The present invention also relates to an improved method for recording digital information on recording media. More particularly, the present invention relates to a method of recording digital information on recording media having a recording layer comprising a mutable dye which layer is mutable or erasable by selectively exposing portions of the recording layer to a specific wavelength of ultraviolet radiation, yet the unexposed portions are color-stable in sunlight or artificial light.

Background of the Invention

It is known in the art to create a digital recording medium comprising a substrate having a layer of a colored, photobleachable composition thereon. Information is recorded on the recording medium by selectively exposing portions of the recording medium to light to thereby initiate a chemical reaction which results in decomposition of the coloring agent contained therein. Examples of such prior art recording media are disclosed in U.S. Pat. No. 5,312,713; U.S. Pat. No. 4,954,380 and Japanese patent application No. 01-342989 (the disclosures of which are all incorporated herein by reference). Examples of such digital recording media include, optical disks, such as compact discs, which are a read-only, non-erasable media for storing information, such as digitized music, video, computer data, and combinations thereof, and writable optical disks, such as write once, read many times "WORM disks."

U.S. Pat. No. 5,312,713 relates to an information recording medium, such as an optical disk. The patent discloses a substrate

upon which is disposed a recording layer. The recording layer comprises a mixture of organic polysilane and an oxo metallic phthalocyanine dye. An ultraviolet light source is selectively irradiated on portions of the recording layer. The irradiation causes a photo decomposition of the organic polysilane. Then, the entire recording layer is heated to a temperature equal to or greater than the glass transition point of the organic polysilane so that the decomposition product produced by the photodecomposition contacts the oxo metallic phthalocyanine pigment which causes the decoloring reaction of the pigment. Thereby, only the portion of the pigment in the recording layer which was irradiated by the ultraviolet light is decolorized; the non-irradiated portion retains it color. The information recorded on the recording layer can be read by detecting the difference among the absorbency of each portion (i.e., between irradiated and non-irradiated portions) by scanning the recording layer with low-energy laser beams.

U.S. Pat. No. 4,954,380 relates to an optical recording medium. This patent discloses a transparent substrate upon which is coated an optical recording layer which includes a bleachable organic dye which is bleachable under ultraviolet radiation, such as cyanine dyes, xanthene dyes and azine dyes. A photomask having a transparent tracking pattern is then placed over the recording layer and the mask is irradiated with ultraviolet light. The exposed portion of the recording layer is bleached due to photochemical decomposition of the organic dyes in the recording layer. As a result, there is formed in the recording layer a tracking region having different optical characteristics from the non-exposed region.

Japanese patent application No. 01-342989 relates to an optical recording medium. The recording medium comprises a base, a recording layer, a reflective layer and a protective coating layer. The recording layer comprises a coloring matter, such as a cyanine dye having a maximum absorbency of 600-900 nm, and a

photobleachable coloring matter, such as an azo dye having a maximum absorbency of 350-600 nm.

A major problem with colorants used in information storage media, such as optical disks, is that they tend to fade when exposed to sunlight or artificial light. It is believed that most of the fading of colorants when exposed to light is due to photodegradation mechanisms. These degradation mechanisms include oxidation or reduction of the colorants depending upon the environmental conditions in which the colorant is placed. Fading of a colorant also depends upon the substrate upon which they reside.

Product analysis of stable photoproducts and intermediates has revealed several important modes of photodecomposition. These include electron ejection from the colorant, reaction with ground-state or excited singlet state oxygen, cleavage of the central carbon-phenyl ring bonds to form amino substituted benzophenones, such as triphenylmethane dyes, reduction to form the colorless leuco dyes and electron or hydrogen atom abstraction to form radical intermediates.

Various factors such as temperature, humidity, gaseous reactants, including O_2, O_3, SO_2, and NO_2, and water soluble, nonvolatile photodegradation products have been shown to influence fading of colorants. The factors that effect colorant fading appear to exhibit a certain amount of interdependence. It is due to this complex behavior that observations for the fading of a particular colorant on a particular substrate cannot be applied to colorants and substrates in general.

Under conditions of constant temperature it has been observed that an increase in the relative humidity of the atmosphere increases the fading of a colorant for a variety of colorant-substrate systems (e.g., McLaren, K., *J. Soc. Dyers Colour*, 1956, 72, 527). For example, as the relative humidity of the atmosphere increases, a fiber may swell because the moisture content of the fiber increases. This aids diffusion of gaseous reactants through the substrate structure.

The ability of a light source to cause photochemical change in a colorant is also dependent upon the spectral distribution of the light source, in particular the proportion of radiation of wavelengths most effective in causing a change in the colorant and the quantum yield of colorant degradation as a function of wavelength. On the basis of photochemical principles, it would be expected that light of higher energy (short wavelengths) would be more effective at causing fading than light of lower energy (long wavelengths). Studies have revealed that this is not always the case. Over 100 colorants of different classes were studied and found that generally the most unstable were faded more efficiently by visible light while those of higher lightfastness were degraded mainly by ultraviolet light (McLaren, K., *J. Soc. Dyers Colour*, 1956, 72, 86).

The influence of a substrate on colorant stability can be extremely important. Colorant fading may be retarded or promoted by some chemical group within the substrate. Such a group can be a ground-state species or an excited-state species. The porosity of the substrate is also an important factor in colorant stability. A high porosity can promote fading of a colorant by facilitating penetration of moisture and gaseous reactants into the substrate. A substrate may also act as a protective agent by screening the colorant from light of wavelengths capable of causing degradation.

The purity of the substrate is also an important consideration whenever the photochemistry of dyed technical polymers is considered. For example, technical-grade cotton, viscose rayon, polyethylene, polypropylene, and polyisoprene are known to contain carbonyl group impurities. These impurities absorb light of wavelengths greater than 300 nm, which are present in sunlight, and so, excitation of these impurities may lead to reactive species capable of causing colorant fading (van Beek, H.C.A., *Col. Res. Appl.*, 1983, 8(3), 176).

Therefore, for all of these reasons, there exists a great need for a digital information recording medium and for a method of

recording digital information on a recording medium which medium is more stable to the effects of both sunlight and artificial light.

Summary of the Invention

The present invention addresses the needs described above by providing a recording medium which is stabilized against radiation including radiation in the visible wavelength range and in which the light-stable colored recording layer is mutable by exposure to certain narrow bandwidths of radiation; particularly, ultraviolet radiation. Thus, the present invention provides a recording layer comprising a colorant which, in the presence of an ultraviolet radiation transorber, is mutable when exposed to a specific wavelength of ultraviolet radiation, while at the same time, provides light stability to the colorant when the composition is exposed to sunlight or artificial light.

Specifically, the recording layer of the present invention includes a colorant and a radiation transorber. When the recording layer of the present invention is exposed to sunlight or artificial light, the colorant therein is stabilized so that it does not fade in the light. The radiation transorber may be any material which is adapted to absorb radiation and interact with the colorant to effect the mutation of the colorant. Generally, the radiation transorber contains a photoreactor and a wavelength-specific sensitizer. The wavelength-specific sensitizer generally absorbs radiation having a specific wavelength, and therefore a specific amount of energy, and transfers the energy to the photoreactor. It is desirable that the mutation of the colorant be irreversible.

The present invention also relates to recording medium colorant compositions having improved stability, wherein the colorant is associated with a modified photoreactor. It has been determined that conventional photoreactors, which normally contain a carbonyl group with a functional group on the carbon alpha to the carbonyl group, acquire the ability to stabilize

colorants when the functional group on the alpha carbon is removed via dehydration.

Accordingly, the present invention also includes a novel method of dehydrating photoreactors that have a hydroxyl group in the alpha position to a carbonyl group. This reaction is necessary to impart the colorant stabilizing capability to the photoreactor. The novel method of dehydrating photoreactors that have a hydroxyl group in the alpha position to a carbonyl group can be used with a wide variety of photoreactors to provide the colorant stabilizing capability to the photoreactor. The resulting modified photoreactor can optionally be linked to a wavelength-selective sensitizer to impart the capability of decolorizing a colorant when exposed to a predetermined narrow wavelength of electromagnetic radiation. Accordingly, the present invention provides a photoreactor capable of stabilizing a colorant with which it is admixed.

As stated above, the mixture of colorant and radiation transorber is mutable upon exposure to radiation. The photoreactor may or may not be modified as described above to impart stability when admixed to a colorant. In one embodiment, an ultraviolet radiation transorber is adapted to absorb ultraviolet radiation and interact with the colorant to effect the irreversible mutation of the colorant. It is desirable that the ultraviolet radiation transorber absorb ultraviolet radiation at a wavelength of from about 4 to about 300 nanometers. It is even more desirable that the ultraviolet radiation transorber absorb ultraviolet radiation at a wavelength of 100 to 300 nanometers. The colorant in combination with the ultraviolet radiation transorber remains stable when exposed to sunlight or artificial light. If the photoreactor is modified as described above, the colorant has improved stability when exposed to sunlight or artificial light.

In another embodiment of the present invention, the colored composition of the present invention may also contain a molecular includant having a chemical structure which defines at

least one cavity. The molecular includants include, but are not limited to, clathrates, zeolites, and cyclodextrins. Each of the colorant and ultraviolet radiation transorber or modified photoreactor can be associated with one or more molecular includant. The includant can have multiple radiation transorbers associated therewith (see co-pending U.S. Patent Application Serial No. 08/359,670). In other embodiments, the includant can have many modified photoreactors associated therewith.

In some embodiments, the colorant is at least partially included within a cavity of the molecular includant and the ultraviolet radiation transorber or modified photoreactor is associated with the molecular includant outside of the cavity. In some embodiments, the ultraviolet radiation transorber or modified photoreactor is covalently coupled to the outside of the molecular includant.

The present invention also relates to a method of mutating the colorant associated with the composition of the present invention. The method comprises irradiating a composition containing a mutable colorant and an ultraviolet radiation transorber with ultraviolet radiation at a dosage level sufficient to mutate the colorant. As stated above, in some embodiments the composition further includes a molecular includant. In another embodiment, the composition is applied to a substrate before being irradiated with ultraviolet radiation. It is desirable that the mutated colorant is stable.

The present invention also relates to a method of recording information on a recording medium comprising a colored recording layer. The colored recording layer comprises a colorant and a radiation transorber as described above. Information is recorded on the recording layer by mutating the colorant in the colored recording layer of the present invention. The method comprises selectively irradiating the colored recording layer with ultraviolet radiation at a dosage level sufficient to mutate or erase (i.e., decolorize) the colorant. As

stated above, in some embodiments the recording layer further includes a molecular includant.

Accordingly, the present invention provides an improved information recording medium and an improved method of recording information. Also, the present invention provides an information recording medium having a mutable colored recording layer thereon which layer is color-stable when exposed to sunlight or artificial light. The present invention further provides an information recording medium having a mutable colored recording layer thereon which layer can be selectively decolorized by exposure to a predetermined relatively narrow wavelength of electromagnetic radiation.

The present invention also provides an information recording medium having a mutable colored recording layer thereon which layer does not require a complicated developing process. Further, the present invention provides an improved optical disk for recording digital information, such as music, video, computer data, and the like, which is relatively easy to fabricate.

These and other objects, features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended drawing and claims.

Brief Description of the Drawing

Fig. 1 illustrates an ultraviolet radiation transorber/mutable colorant/molecular includant complex wherein the mutable colorant is malachite green, the ultraviolet radiation transorber is IRGACURE 184 (1-hydroxycyclohexyl phenyl ketone), and the molecular includant is ß-cyclodextrin.

Fig. 2 illustrates an ultraviolet radiation transorber/mutable colorant/molecular includant complex wherein the mutable colorant is Victoria Pure Blue BO (Basic Blue 7), the ultraviolet radiation transorber is IRGACURE 184 (1-hydroxycyclohexyl phenyl ketone), and the molecular includant is ß-cyclodextrin.

Fig. 3 is a plot of the average number of ultraviolet radiation transorber molecules which are covalently coupled to each molecule of a molecular includant in several colored compositions, which number also is referred to by the term, "degree of substitution," versus the decolorization time upon exposure to 222-nanometer excimer lamp ultraviolet radiation.

Fig. 4 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the twelve numbers represent the locations where twelve intensity measurements were obtained approximately 5.5 centimeters from the excimer lamps.

Fig. 5 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the nine numbers represent the locations where nine intensity measurements were obtained approximately 5.5 centimeters from the excimer lamps.

Fig. 6 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the location of the number "1" denotes the location where ten intensity measurements were obtained from increasing distances from the lamps at that location. (The measurements and their distances from the lamp are summarized in Table 12.)

Fig. 7 is a plan view of a disclosed embodiment of an optical disc in accordance with the present invention.

Fig. 8 is a cross-sectional schematic view of the optical disc shown in Fig. 7 taken along the line 2--2 and also showing a disclosed embodiment of the information recording/reading system of the present invention.

Fig. 9 is a cross-sectional schematic view of an alternate disclosed embodiment of the information recording/reading system of the present invention.

Fig. 10 is a partial detail view of the optical disk shown in Fig. 7.

Fig. 11 is a cross-sectional schematic view of an alternate disclosed embodiment of the information recording/reading system of the present invention.

Detailed Description of the Invention

The present invention relates in general to a light-stable colorant system that is mutable by exposure to narrow band-width ultraviolet radiation and to a recording medium employing such a colorant system. The present invention more particularly relates to a composition comprising a colorant which, in the presence of a radiation transorber, is stable under ordinary light but is mutable when exposed to specific, narrow band-width radiation. The radiation transorber is capable of absorbing radiation and interacting with the colorant to effect a mutation of the colorant. The radiation transorber may be any material which is adapted to absorb radiation and interact with the colorant to effect the mutation of the colorant. Generally, the radiation transorber contains a photoreactor and a wavelength-specific sensitizer. The wavelength-specific sensitizer generally absorbs radiation having a specific wavelength, and therefore a specific amount of energy, and transfers the energy to the photoreactor. It is desirable that the mutation of the colorant be irreversible.

The present invention also relates to colorant compositions having improved stability, wherein the colorant is associated with a modified photoreactor. It has been determined that conventional photoreactors which normally contain a carbonyl group with a functional group on the carbon alpha to the carbonyl group acquire the ability to stabilize colorants when the functional group on the alpha carbon is removed. Accordingly, the present invention also includes a novel method of dehydrating photoreactors that have a hydroxyl group in the alpha position to a carbonyl group. This reaction is necessary to impart the colorant stabilizing capability to the photoreactor. The novel method of dehydrating photoreactors that have a hydroxyl group in the alpha position to a carbonyl group can be used with a wide

variety of photoreactors to provide the colorant stabilizing capability to the photoreactor. The resulting modified photoreactor can optionally be linked to wavelength-selective sensitizer to impart the capability of decolorizing a colorant when exposed to a predetermined narrow wavelength of electromagnetic radiation. Accordingly, the present invention provides a photoreactor capable of stabilizing a colorant that it is admixed with.

In certain embodiments of the present invention, the colorant and radiation transorber is mutable upon exposure to radiation. In this embodiment, the photoreactor may or may not be modified as described above to impart stability when admixed to a colorant. In one embodiment, an ultraviolet radiation transorber is adapted to absorb ultraviolet radiation and interact with the colorant to effect the irreversible mutation of the colorant. It is desirable that the ultraviolet radiation transorber absorb ultraviolet radiation at a wavelength of from about 4 to about 300 nanometers. If the photoreactor in the radiation transorber is modified as described above, the colorant has improved stability when exposed to sunlight or artificial light.

The present invention also relates to a method of mutating the colorant in the composition of the present invention. The method comprises irradiating a composition containing a mutable colorant and a radiation transorber with radiation at a dosage level sufficient to mutate the colorant.

The present invention further relates to a method of stabilizing a colorant comprising associating the modified photoreactor described above with the colorant. Optionally, the photoreactor may be associated with a wavelength-selective sensitizer, or the photoreactor may be associated with a molecular includant, or both.

With reference to the drawing in which like number indicate like elements throughout the several views, it will be seen that there is a compact disc 10 comprising a plastic substrate 12 and a recording layer 14 disposed thereon.

The recording layer 14 comprises a colored composition comprising a colorant which, in the presence of a radiation transorber, is stable under ordinary light but is mutable when exposed to specific, narrow band-width radiation. Desirably , the radiation transorber is an ultraviolet radiation transorber. The ultraviolet radiation transcrber is capable of absorbing ultraviolet radiation and interacting with the colorant to effect a mutation of the colorant. Optionally, a molecular includant can be included in the composition which provides a more efficient mutable colorant and a more stable colorant to sunlight and ordinary artificial light.

The term "composition" and such variations as "colored composition" are used herein to mean a colorant, and a radiation transorber. A radiation transorber is comprised of a photoreactor and a wavelength-selective sensitizer. The photoreactor may be any of the photoreactors listed below, including conventional photoreactors, and modified photoreactors as described below. When reference is being made to a colored composition which is adapted for a specific application, the term "composition-based" is used as a modifier to indicate that the material includes a colorant, an ultraviolet radiation transorber, and, optionally, a molecular includant. Optionally, the material may include other components as discussed below.

As used herein, the term "colorant" is meant to include, without limitation, any material which, in the presence of a radiation transorber, is adapted upon exposure to specific radiation to be mutable. The colorant will typically be an organic material, such as an organic colorant or pigment. Desirably, the colorant will be substantially transparent to, that is, will not significantly interact with, the ultraviolet radiation to which it is exposed. The term is meant to include a single material or a mixture of two or more materials.

As used herein, the term "irreversible" means that the colorant will not revert to its original color when it no longer is exposed to ultraviolet radiation.

The term “radiation transorber” is used herein to mean any material which is adapted to absorb radiation at a specific wavelength and interact with the colorant to affect the mutation of the colorant and, at the same time, protect the colorant from fading in sunlight or artificial light. The term “ultraviolet radiation transorber” is used herein to mean any material which is adapted to absorb ultraviolet radiation and interact with the colorant to effect the mutation of the colorant. In some embodiments, the ultraviolet radiation transorber may be an organic compound. Where the radiation transorber is comprised of a wavelength-selective sensitizer and a photoreactor, the photoreactor may optionally be modified as described below.

The term “compound” is intended to include a single material or a mixture of two or more materials. If two or more materials are employed, it is not necessary that all of them absorb radiation of the same wavelength. As discussed more fully below, a radiation transorber is comprised of a photoreactor and a wavelength selective sensitizer. The radiation transorber has the additional property of making the colorant with which the radiation transorber is associated light stable to sunlight or artificial light.

The term “light-stable” is used herein to mean that the colorant, when associated with the radiation transorber or modified photoreactor, is more stable to light, including, but not limited to, sunlight or artificial light, than when the colorant is not associated with these compounds.

The term “molecular includant,” as used herein, is intended to mean any substance having a chemical structure which defines at least one cavity. That is, the molecular includant is a cavity-containing structure. As used herein, the term “cavity” is meant to include any opening or space of a size sufficient to accept at least a portion of one or both of the colorant and the ultraviolet radiation transorber.

The term "functionalized molecular includant" is used herein to mean a molecular includant to which one or more

molecules of an ultraviolet radiation transorber are covalently coupled to each molecule of the molecular includant. The term "degree of substitution" is used herein to refer to the number of these molecules or leaving groups (defined below) which are covalently coupled to each molecule of the molecular includant.

The term "derivatized molecular includant" is used herein to mean a molecular includant having more than two leaving groups covalently coupled to each molecule of molecular includant. The term "leaving group" is used herein to mean any leaving group capable of participating in a bimolecular nucleophilic substitution reaction.

The term "artificial light" is used herein to mean light having a relatively broad bandwidth that is produced from conventional light sources, including, but not limited to, conventional incandescent light bulbs and fluorescent light bulbs.

The term "ultraviolet radiation" is used herein to mean electromagnetic radiation having wavelengths in the range of from about 4 to about 400 nanometers. The especially desirable ultraviolet radiation range for the present invention is between approximately 100 to 375 nanometers. Thus, the term includes the regions commonly referred to as ultraviolet and vacuum ultraviolet. The wavelength ranges typically assigned to these two regions are from about 180 to about 400 nanometers and from about 100 to about 180 nanometers, respectively.

The term "thereon" is used herein to mean thereon or therein. For example, the present invention includes a substrate having a colored composition thereon. According to the definition of "thereon" the colored composition may be present on the substrate or it may be in the substrate.

The term "mutable," with reference to the colorant, is used to mean that the absorption maximum of the colorant in the visible region of the electromagnetic spectrum is capable of being mutated or changed by exposure to radiation, desirably ultraviolet radiation, when in the presence of the radiation transorber. In general, it is only necessary that such absorption maximum be

mutated to an absorption maximum which is different from that of the colorant prior to exposure to the ultraviolet radiation, and that the mutation be irreversible. Thus, the new absorption maximum can be within or outside of the visible region of the electromagnetic spectrum. In other words, the colorant can mutate to a different color or be rendered colorless. The latter is also desirable when the colorant is used in data processing forms for use with photo-sensing apparatus that detect the presence of indicia at indicia-receiving locations of the form.

In several embodiments, the radiation transorber molecule, the wavelength-selective sensitizer, or the photoreactor may be associated with a molecular includant. It is to be noted that in all the formulas, the number of such molecules can be between approximately 1 and approximately 21 molecules per molecular includant. Of course, in certain situations, there can be more than 21 molecules per molecular includant molecule. Desirably, there are more than three of such molecules per molecular includant.

The degree of substitution of the functionalized molecular includant may be in a range of from 1 to approximately 21. As another example, the degree of substitution may be in a range of from 3 to about 10. As a further example, the degree of substitution may be in a range of from about 4 to about 9.

The colorant is associated with the functionalized molecular includant. The term "associated" in its broadest sense means that the colorant is at least in close proximity to the functionalized molecular includant. For example, the colorant may be maintained in close proximity to the functionalized molecular includant by hydrogen bonding, van der Waals forces, or the like. Alternatively, the colorant may be covalently bonded to the functionalized molecular includant, although this normally is neither desired nor necessary. As a further example, the colorant may be at least partially included within the cavity of the functionalized molecular includant.

The examples below disclose methods of preparing and associating these colorants and ultraviolet radiation transorbers to

beta-cyclodextrins. For illustrative purposes only, Examples 1, 2, 6, and 7 disclose one or more methods of preparing and associating colorants and ultraviolet radiation transorbers to cyclodextrins.

In those embodiments of the present invention in which the ultraviolet radiation transorber is covalently coupled to the molecular includant, the efficiency of energy transfer from the ultraviolet radiation transorber to the colorant is, at least in part, a function of the number of ultraviolet radiation transorber molecules which are attached to the molecular includant. It now is known that the synthetic methods described above result in covalently coupling an average of two transorber molecules to each molecule of the molecular includant. Because the time required to mutate the colorant should, at least in part, be a function of the number of ultraviolet radiation transorber molecules coupled to each molecule of molecular includant, there is a need for an improved colored composition in which an average of more than two ultraviolet radiation transorber molecules are covalently coupled to each molecule of the molecular includant.

Accordingly, the present invention also relates to a composition which includes a colorant and a functionalized molecular includant. For illustrative purposes only, Examples 12 through 19, and 21 through 22 disclose other methods of preparing and associating colorants and ultraviolet radiation transorbers to cyclodextrins, wherein more than two molecules of the ultraviolet radiation transorber are covalently coupled to each molecule of the molecular includant.

The present invention also provides a method of making a functionalized molecular includant. The method of making a functionalized molecular includant involves the steps of providing a derivatized ultraviolet radiation transorber having a nucleophilic group, providing a derivatized molecular includant having more than two leaving groups per molecule, and reacting the derivatized ultraviolet radiation transorber with the

derivatized molecular includant under conditions sufficient to result in the covalent coupling of an average of more than two ultraviolet radiation transorber molecules to each molecular includant molecule. By way of example, the derivatized ultraviolet radiation transorber may be 2-[*p*-(2-methyl-2-mercaptomethylpropionyl)phenoxy]ethyl 1,3-dioxo-2-isoindoline-acetate. As another example, the derivatized ultraviolet radiation transorber may be 2-mercaptomethyl-2-methyl-4'-[2-[*p*-(3-oxobutyl)phenoxy]ethoxy]propiophenone.

In general, the derivatized ultraviolet radiation transorber and the derivatized molecular includant are selected to cause the covalent coupling of the ultraviolet radiation transorber to the molecular includant by means of a bimolecular nucleophilic substitution reaction. Consequently, the choice of the nucleophilic group and the leaving groups and the preparation of the derivatized ultraviolet radiation transorber and derivatized molecular includant, respectively, may be readily accomplished by those having ordinary skill in the art without the need for undue experimentation.

The nucleophilic group of the derivatized ultraviolet radiation transorber may be any nucleophilic group capable of participating in a bimolecular nucleophilic substitution reaction, provided, of course, that the reaction results in the covalent coupling of more than two molecules of the ultraviolet radiation transorber to the molecular includant. The nucleophilic group generally will be a Lewis base, i.e., any group having an unshared pair of electrons. The group may be neutral or negatively charged. Examples of nucleophilic groups include, by way of illustration only, aliphatic hydroxy, aromatic hydroxy, alkoxides, carboxy, carboxylate, amino, and mercapto.

Similarly, the leaving group of the derivatized molecular includant may be any leaving group capable of participating in a bimolecular nucleophilic substitution reaction, again provided that the reaction results in the covalent coupling of more than two molecules of the ultraviolet radiation transorber to the molecular

includant. Examples of leaving groups include, also by way of illustration only, *p*-toluenesulfonates (tosylates), *p*-bromobenzenesulfonates (brosylates), *p*-nitrobenzenesulfonates (nosylates), methanesulfonates (mesylates), oxonium ions, alkyl perchlorates, ammonioalkane sulfonate esters (betylates), alkyl fluorosulfonates, trifluoromethanesulfonates (triflates), nonafluorobutanesulfonates (nonaflates), and 2,2,2-trifluoroethanesulfonates (tresylates).

The reaction of the derivatized ultraviolet radiation transorber with the derivatized molecular includant is carried out in solution. The choice of solvent depends upon the solubilities of the two derivatized species. As a practical matter, a particularly useful solvent is N,N-dimethylformamide (DMF).

The reaction conditions, such as temperature, reaction time, and the like generally are matters of choice based upon the natures of the nucleophilic and leaving groups. Elevated temperatures usually are not required. For example, the reaction temperature may be in a range of from about 0°C to around ambient temperature, i.e., to 20°-25°C.

The preparation of the functionalized molecular includant as described above generally is carried out in the absence of the colorant. However, the colorant may be associated with the derivatized molecular includant before reacting the derivatized ultraviolet radiation transorber with the derivatized molecular includant, particularly if a degree of substitution greater than about three is desired. When the degree of substitution is about three, it is believed that the association of the colorant with the functionalized molecular includant still may permit the colorant to be at least partially included in a cavity of the functionalized molecular includant. At higher degrees of substitution, such as about six, steric hindrance may partially or completely prevent the colorant from being at least partially included in a cavity of the functionalized molecular includant. Consequently, the colorant may be associated with the derivatized molecular includant which normally will exhibit little, if any, steric

hindrance. In this instance, the colorant will be at least partially included in a cavity of the derivatized molecular includant. The above-described bimolecular nucleophilic substitution reaction then may be carried out to give a colored composition of the present invention in which the colorant is at least partially included in a cavity of the functionalized molecular includant.

As stated above, the present invention provides compositions comprising a colorant which, in the presence of a radiation transorber, is mutable when exposed to a specific wavelength of radiation, while at the same time, provides light stability to the colorant with respect to sunlight and artificial light. Desirably, the mutated colorant will be stable, i.e., not appreciably adversely affected by radiation normally encountered in the environment, such as natural or artificial light and heat. Thus, desirably, a colorant rendered colorless will remain colorless indefinitely.

The dye, for example, may be an organic dye. Organic dye classes include, by way of illustration only, triarylmethyl dyes, such as Malachite Green Carbinol base {4-(dimethylamino)-α-[4-(dimethylamino)phenyl]-α-phenylbenzene-methanol}, Malachite Green Carbinol hydrochloride {N-4-[[4-(dimethylamino)phenyl]phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[*p*-(dimethylamino)phenyl]phenylmethylium chloride}, and Malachite Green oxalate {N-4-[[4-(dimethylamino)phenyl]phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methylmethanaminium chloride or bis[*p*-(dimethyl-amino)phenyl]phenylmethylium oxalate}; monoazo dyes, such as Cyanine Black, Chrysoidine [Basic Orange 2; 4-(phenylazo)-1,3-benzenediamine monohydrochloride], Victoria Pure Blue BO, Victoria Pure Blue B, basic fuschin and ß-Naphthol Orange; thiazine dyes, such as Methylene Green, zinc chloride double salt [3,7-bis(dimethylamino)-6-nitrophenothiazin-5-ium chloride, zinc chloride double salt]; oxazine dyes, such as Lumichrome (7,8-dimethylalloxazine); naphthalimide dyes, such as Lucifer Yellow

CH {6-amino-2-[(hydrazinocarbonyl)amino]-2,3-dihydro-1,3-dioxo-1H-benz[de]isoquinoline-5,8-disulfonic acid dilithium salt}; azine dyes, such as Janus Green B {3-(diethylamino)-7-[[4-(dimethylamino)phenyl]azo]-5-phenylphenazinium chloride}; cyanine dyes, such as Indocyanine Green {Cardio-Green or Fox Green; 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide inner salt sodium salt}; indigo dyes, such as Indigo {Indigo Blue or Vat Blue 1; 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one}; coumarin dyes, such as 7-hydroxy-4-methylcoumarin (4-methylumbelliferone); benzimidazole dyes, such as Hoechst 33258 [bisbenzimide or 2-(4-hydroxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5-bi-1H-benzimidazole trihydrochloride pentahydrate]; paraquinoidal dyes, such as Hematoxylin {Natural Black 1; 7,11b-dihydrobenz[b]indeno[1,2-d]pyran-3,4,6a,9,10(6H)-pentol}; fluorescein dyes, such as Fluoresceinamine (5-aminofluorescein); diazonium salt dyes, such as Diazo Red RC (Azoic Diazo No. 10 or Fast Red RC salt; 2-methoxy-5-chlorobenzenediazonium chloride, zinc chloride double salt); azoic diazo dyes, such as Fast Blue BB salt (Azoic Diazo No. 20; 4-benzoylamino-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt); phenylenediamine dyes, such as Disperse Yellow 9 [N-(2,4-dinitrophenyl)-1,4-phenylenediamine or Solvent Orange 53]; diazo dyes, such as Disperse Orange 13 [Solvent Orange 52; 1-phenylazo-4-(4-hydroxyphenylazo)naphthalene]; anthraquinone dyes, such as Disperse Blue 3 [Celliton Fast Blue FFR; 1-methylamino-4-(2-hydroxyethylamino)-9,10-anthraquinone], Disperse Blue 14 [Celliton Fast Blue B; 1,4-bis(methylamino)-9,10-anthraquinone], and Alizarin Blue Black B (Mordant Black 13); trisazo dyes, such as Direct Blue 71 {Benzo Light Blue FFL or Sirius Light Blue BRR; 3-[(4-[(4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo]-6-sulfo-1-naphthalenyl)azo]-1-naphthalenyl)azo]-1,5-naphthalenedisulfonic acid tetrasodium salt}; xanthene dyes, such as 2,7-dichlorofluorescein; proflavine dyes,

such as 3,6-diaminoacridine hemisulfate (Proflavine); sulfonaphthalein dyes, such as Cresol Red (o-cresolsulfonaphthalein); phthalocyanine dyes, such as Copper Phthalocyanine {Pigment Blue 15; (SP-4-1)-[29H,31H-phthalocyanato(2-)-N^{29},N^{30},N^{31},N^{32}]copper}; carotenoid dyes, such as trans-ß-carotene (Fooα Orange 5); carminic acid dyes, such as Carmine, the aluminum or calcium-aluminum lake of carminic acid (7-a-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarbonylic acid); azure dyes, such as Azure A [3-amino-7-(dimethylamino)phenothiazin-5-ium chloride or 7-(dimethylamino)-3-imino-3H-phenothiazine hydrochloride]; and acridine dyes, such as Acridine Orange [Basic Orange 14; 3,8-bis(dimethylamino)acridine hydrochloride, zinc chloride double salt] and Acriflavine (Acriflavine neutral; 3,6-diamino-10-methylacridinium chloride mixture with 3,6-acridinediamine).

The present invention includes unique compounds, namely, radiation transorbers, that are capable of absorbing narrow ultraviolet wavelength radiation, while at the same time, imparting light-stability to a colorant with which the compounds are associated. The compounds are synthesized by combining a wavelength-selective sensitizer and a photoreactor. The photoreactors oftentimes do not efficiently absorb high energy radiation. When combined with the wavelength-selective sensitizer, the resulting compound is a wavelength specific compound that efficiently absorbs a very narrow spectrum of radiation. The wavelength-selective sensitizer may be covalently coupled to the photoreactor.

By way of example, the wavelength-selective sensitizer may be selected from the group consisting of phthaloylglycine and 4-(4-oxyphenyl)-2-butanone. As another example, the photoreactor may be selected from the group consisting of 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methylpropan-1-one and cyclohexyl-phenyl ketone ester. Other photoreactors are listed by way of example, in the detailed description below regarding the

improved stabilized composition of the present invention. As a further example, the ultraviolet radiation transorber may be 2-[*p*-2-methyllactoyl)phenoxy]ethyl 1,3-dioxo-2-isoin-dolineacetate. As still another example, the ultraviolet radiation transorber may be 2-hydroxy-2-methyl-4'-2-[*p*-(3-oxobutyl)phenoxy]propiophenone.

Although the colorant and the ultraviolet radiation transorber have been described as separate compounds, they can be part of the same molecule. For example, they can be covalently coupled to each other, either directly, or indirectly through a relatively small molecule, or spacer. Alternatively, the colorant and ultraviolet radiation transorber can be covalently coupled to a large molecule, such as an oligomer or a polymer. Further, the colorant and ultraviolet radiation transorber may be associated with a large molecule by van der Waals forces, and hydrogen bonding, among other means. Other variations will be readily apparent to those having ordinary skill in the art.

For example, in an embodiment of the composition of the present invention, the composition further comprises a molecular includant. Thus, the cavity in the molecular includant can be a tunnel through the molecular includant or a cave-like space or a dented-in space in the molecular includant. The cavity can be isolated or independent, or connected to one or more other cavities.

The molecular includant can be inorganic or organic in nature. In certain embodiments, the chemical structure of the molecular includant is adapted to form a molecular inclusion complex. Examples of molecular includants are, by way of illustration only, clathrates or intercalates, zeolites, and cyclodextrins. Examples of molecular includants are, by way of illustration only, clathrates or intercalates, zeolites, and cyclodextrins. Examples of cyclodextrins include, but are not limited to, α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin, hydroxypropyl β-cyclodextrin, hydroxyethyl β-cyclodextrin, sulfated β-cyclodextrin, hydroxyethyl α cyclodextrin,

carboxymethyle α cyclodextrin, carboxymethyl β cyclodextrin, carboxymethyl γ cyclodextrin, octyl succinated α cyclodextrin, octyl succinated β cyclodextrin, octyl succinated γ cyclodextrin and sulfated β and γ-cyclodextrin (American Maize-Products Company, Hammond, Indiana).

The desired molecular includant is α-cyclodextrin. More particularly, in some embodiments, the molecular includant is an α -cyclodextrin. In other embodiments, the molecular includant is a beta-cyclodextrin. Although not wanting to be bound by the following theory, it is believed that the closer the transorber molecule is to the mutable colorant on the molecular includant, the more efficient the interaction with the colorant to effect mutation of the colorant. Thus, the molecular includant with functional groups that can react with and bind the transorber molecule and that are close to the binding site of the mutable colorant are the more desirable molecular includants.

In some embodiments, the colorant and the ultraviolet radiation transorber are associated with the molecular includant. The term "associated", in its broadest sense, means that the colorant and the ultraviolet radiation transorber are at least in close proximity to the molecular includant. For example, the colorant and/or the ultraviolet radiation transorber can be maintained in close proximity to the molecular includant by hydrogen bonding, van der Waals forces, or the like. Alternatively, either or both of the colorant and the ultraviolet radiation transorber can be covalently bonded to the molecular includant. In certain embodiments, the colorant will be associated with the molecular includant by means of hydrogen bonding and/or van der Waals forces or the like, while the ultraviolet radiation transorber is covalently bonded to the molecular includant. In other embodiments, the colorant is at least partially included within the cavity of the molecular includant, and the ultraviolet radiation transorber is located outside of the cavity of the molecular includant.

In one embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is crystal violet, the ultraviolet radiation transorber is a dehydrated phthaloylglycine-2959, and the molecular includant is beta-cyclodextrin. In yet another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is crystal violet, the ultraviolet radiation transorber is 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted), and the molecular includant is beta-cyclodextrin.

In another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is malachite green, the ultraviolet radiation transorber is IRGACURE 184, and the molecular includant is beta-cyclodextrin as shown in Figure 1. In still another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is Victoria Pure Blue BO, the ultraviolet radiation transorber is IRGACURE 184, and the molecular includant is beta-cyclodextrin as shown in Figure 2.

The present invention also relates to a method of mutating the colorant in the composition of the present invention. Briefly described, the method comprises irradiating a composition containing a mutable colorant and a radiation transorber with radiation at a dosage level sufficient to mutate the colorant. As stated above, in one embodiment the composition further includes a molecular includant. In another embodiment, the composition is applied to a substrate before being irradiated with ultraviolet radiation.

The radiation to which the photoreactor composition is exposed may have a wavelength of from about 4 to about 1000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation, visible radiation, and near infrared radiation. The radiation may have a wavelength of from about 100 to about 900 nanometers.

Desirably, the composition of the present invention is irradiated with ultraviolet radiation having a wavelength of from about 4 to about 400 nanometers. It is more desirable that the radiation has a wavelength of between about 100 to 375 nanometers. Especially desirable radiation is incoherent, pulsed ultraviolet radiation produced by a dielectric barrier discharge lamp. Even more desirably, the dielectric barrier discharge lamp produces radiation having a narrow bandwidth.

The amount or dosage level of ultraviolet radiation that the colorant of the present invention is exposed to will generally be that amount which is necessary to mutate the colorant. The amount of ultraviolet radiation necessary to mutate the colorant can be determined by one of ordinary skill in the art using routine experimentation. Power density is the measure of the amount of radiated electromagnetic power traversing a unit area and is usually expressed in watts per centimeter squared (W/cm^2). The power density level range is between approximately 5 mW/cm^2 and 15 mW/cm^2, more particularly 8 to 10 mW/cm^2. The dosage level, in turn, typically is a function of the time of exposure and the intensity or flux of the radiation source which irradiates the colored composition. The latter is affected by the distance of the composition from the source and, depending upon the wavelength range of the ultraviolet radiation, can be affected by the atmosphere between the radiation source and the composition. Accordingly, in some instances it may be appropriate to expose the composition to the radiation in a controlled atmosphere or in a vacuum, although in general neither approach is desired.

With regard to the mutation properties of the present invention, photochemical processes involve the absorption of light quanta, or photons, by a molecule, e.g., the ultraviolet radiation transorber, to produce a highly reactive electronically excited state. However, the photon energy, which is proportional to the wavelength of the radiation, cannot be absorbed by the molecule unless it matches the energy difference between the unexcited, or original, state and an excited state. Consequently, while the

wavelength range of the ultraviolet radiation to which the colored composition is exposed is not directly of concern, at least a portion of the radiation must have wavelengths which will provide the necessary energy to raise the ultraviolet radiation transorber to an energy level which is capable of interacting with the colorant.

It follows, then, that the absorption maximum of the ultraviolet radiation transorber ideally will be matched with the wavelength range of the ultraviolet radiation to increase the efficiency of the mutation of the colorant. Such efficiency also will be increased if the wavelength range of the ultraviolet radiation is relatively narrow, with the maximum of the ultraviolet radiation transorber coming within such range. For these reasons, especially suitable ultraviolet radiation has a wavelength of from about 100 to about 375 nanometers. Ultraviolet radiation within this range desirably may be incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

The term "incoherent, pulsed ultraviolet radiation" has reference to the radiation produced by a dielectric barrier discharge excimer lamp (referred to hereinafter as "excimer lamp"). Such a lamp is described, for example, by U. Kogelschatz, "Silent discharges for the generation of ultraviolet and vacuum ultraviolet excimer radiation," Pure & Appl. Chem., 62, No. 9, pp. 1667-1674 (1990); and E. Eliasson and U. Kogelschatz, "UV Excimer Radiation from Dielectric-Barrier Discharges," Appl. Phys. B, 46, pp. 299-303 (1988). Excimer lamps were developed originally by ABB Infocom Ltd., Lenzburg, Switzerland. The excimer lamp technology since has been acquired by Haräus Noblelight AG, Hanau, Germany.

The excimer lamp emits incoherent, pulsed ultraviolet radiation. Such radiation has a relatively narrow bandwidth, i.e., the half width is of the order of approximately 5 to 100 nanometers. Desirably, the radiation will have a half width of the order of approximately 5 to 50 nanometers, and more desirably

will have a half width of the order of 5 to 25 nanometers. Most desirably, the half width will be of the order of approximately 5 to 15 nanometers. This emitted radiation is incoherent and pulsed, the frequency of the pulses being dependent upon the frequency of the alternating current power supply which typically is in the range of from about 20 to about 300 kHz. An excimer lamp typically is identified or referred to by the wavelength at which the maximum intensity of the radiation occurs, which convention is followed throughout this specification. Thus, in comparison with most other commercially useful sources of ultraviolet radiation which typically emit over the entire ultraviolet spectrum and even into the visible region, excimer lamp radiation is substantially monochromatic.

Excimers are unstable molecular complexes which occur only under extreme conditions, such as those temporarily existing in special types of gas discharge. Typical examples are the molecular bonds between two rare gaseous atoms or between a rare gas atom and a halogen atom. Excimer complexes dissociate within less than a microsecond and, while they are dissociating, release their binding energy in the form of ultraviolet radiation. Known excimers; in general, emit in the range of from about 125 to about 360 nanometers, depending upon the excimer gas mixture.

In addition to excimer lamps, it is specifically contemplated that the colored composition of the present invention can be mutated with the light from a laser, particularly, an excimer laser. An excimer laser is a laser containing a noble gas, such as helium or neon, or halides of the noble gases, as its active medium. Excimer lasers are pulsed and produce high peak powers in the ultraviolet spectrum.

For example, in one embodiment, the colorant of the present invention is mutated by exposure to 222 nanometer excimer lamps. More particularly, the colorant crystal violet is mutated by exposure to 222 nanometer lamps. Even more particularly, the colorant crystal violet is mutated by exposure to

222 nanometer excimer lamps located approximately 5 to 6 centimeters from the colorant, wherein the lamps are arranged in four parallel columns approximately 30 centimeters long. It is to be understood that the arrangement of the lamps is not critical to this aspect of the invention. Accordingly, one or more lamps may be arranged in any configuration and at any distance which results in the colorant mutating upon exposure to the lamp's ultraviolet radiation. One of ordinary skill in the art would be able to determine by routine experimentation which configurations and which distances are appropriate. Also, it is to be understood that different excimer lamps are to be used with different ultraviolet radiation transorbers. The excimer lamp used to mutate a colorant associated with an ultraviolet radiation transorber should produce ultraviolet radiation of a wavelength that is absorbed by the ultraviolet radiation transorber.

In some embodiments, the molar ratio of ultraviolet radiation transorber to colorant generally will be equal to or greater than about 0.5. As a general rule, the more efficient the ultraviolet radiation transorber is in absorbing the ultraviolet radiation and interacting with, i.e., transferring absorbed energy to, the colorant to effect irreversible mutation of the colorant, the lower such ratio can be. Current theories of molecular photo chemistry suggest that the lower limit to such ratio is 0.5, based on the generation of two free radicals per photon. As a practical matter, however, ratios higher than 1 are likely to be required, perhaps as high as about 10. However, the present invention is not bound by any specific molar ratio range. The important feature is that the transorber is present in an amount sufficient to effect mutation of the colorant.

While the mechanism of the interaction of the ultraviolet radiation transorber with the colorant is not totally understood, it is believed that it may interact with the colorant in a variety of ways. For example, the ultraviolet radiation transorber, upon absorbing ultraviolet radiation, may be converted to one or more free radicals which interact with the colorant. Such free radical-

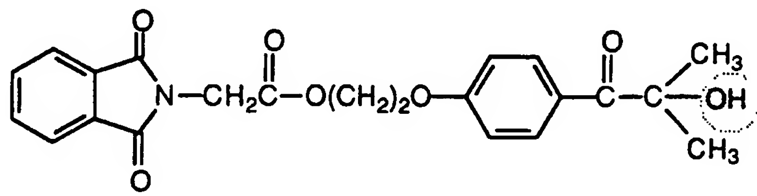
generating compounds typically are hindered ketones, some examples of which include, but are not limited to: benzildimethyl ketal (available commercially as IRGACURE 651, Ciba-Geigy Corporation, Hawthorne, New York); 1-hydroxycyclohexyl phenyl ketone (IRGACURE 500); 2-methyl-1-[4-(methylthio)phenyl]-2-mo:pholino-propan-1-one] (IRGACURE 907); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one (IRGACURE 369); and 1-hydroxycyclohexyl phenyl ketone (IRGACURE 184).

Alternatively, the ultraviolet radiation may initiate an electron transfer or reduction-oxidation reaction between the ultraviolet radiation transorber and the colorant. In this case, the ultraviolet radiation transorber may be, but is not limited to, Michler's ketone (*p*-dimethylaminophenyl ketone) or benzyl trimethyl stannate. Or, a cationic mechanism may be involved, in which case the ultraviolet radiation transorber can be, for example, bis[4-(diphenylsulphonio)phenyl)] sulfide bis-(hexafluorophosphate) (Degacure KI85, Ciba-Geigy Corporation, Hawthorne, New York); Cyracure UVI-6990 (Ciba-Geigy Corporation), which is a mixture of bis[4-(diphenylsulphonio)phenyl] sulfide bis(hexafluorophosphate) with related monosulphonium hexafluorophosphate salts; and n5-2,4-(cyclopentadienyl)[1,2,3,4,5,6-n-(methylethyl)benzene]-iron(II) hexafluorophosphate (IRGACURE 261).

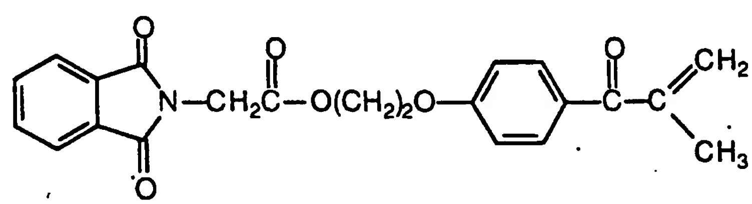
With regard to the light stabilizing activity of the present invention, it has been determined that in some embodiments it is necessary to modify a conventional photoreactor to produce the improved light stable composition of the present invention. The simplest form of the improved light stable composition of the present invention includes a colorant admixed with a photoreactor modified as described below. The modified photoreactor may or may not be combined with a wavelength-selective sensitizer. Many conventional photoreactor molecules have a functional group that is alpha to a carbonyl group. The functional group

includes, but is not limited to, hydroxyl groups, ether groups, ketone groups, and phenyl groups.

For example, a preferred radiation transorber that can be used in the present invention is designated phthaloylglycine-2959 and is represented in the following formula:



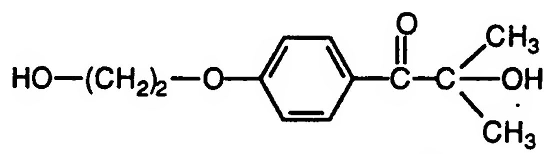
The photoreactor portion of the ultraviolet radiation transorber has a hydroxyl group (shaded portion) alpha to the carbonyl carbon. The above molecule does not light-stabilize a colorant. However, the hydroxyl group can be removed by dehydration (see Example 4 and 5) yielding the compound represented by the following formula:



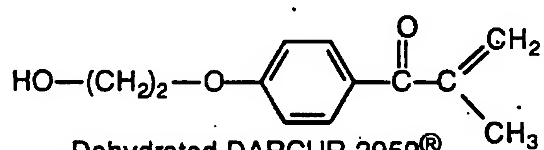
This dehydrated phthaloylglycine-2959 is capable of light-stabilizing a colorant. Thus, it is believed that removal of the functional group alpha to the carbonyl carbon on any photoreactor molecule will impart the light-stabilizing capability to the molecule. While the dehydrated ultraviolet radiation transorber can impart light-stability to a colorant simply by mixing the molecule with the colorant, it has been found that the molecule is much more efficient at stabilizing colorants when it is attached to an includant, such as cyclodextrin, as described herein.

It is to be understood that stabilization of a colorant can be accomplished according to the present invention by utilizing only the modified photoreactor. In other words, a modified

photoreactor without a wavelength selective sensitizer may be used to stabilize a colorant. An example of a photoreactor that is modified according to the present invention is DARCUR 2959. The unmodified DARCUR 2959 and the dehydrated DARCUR 2959 are represented by the following formulas:



Unmodified DARCUR 2959®



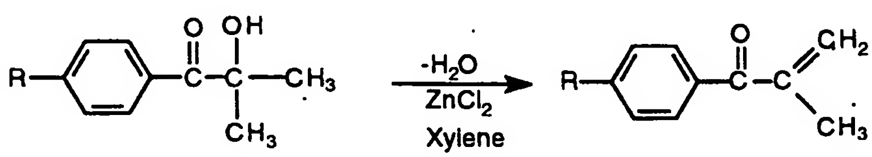
Dehydrated DARCUR 2959®

Other photoreactors can be modified according to the present invention to provide stabilizers for dyes. These photoreactors include, but are not limited to: 1-Hydroxy-cyclohexyl-phenyl ketone ("HCPK") (IRGACURE 184, Ciba-Geigy); α,α-dimethoxy-α-hydroxy acetophenone (DAROCUR 1173, Merck); 1-(4-Isopropylphenyl)-2-hydroxy-2-methyl-propan-1-one (DAROCUR 1116, Merck); 1-[4-(2-Hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one (DAROCUR 2959, Merck); Poly[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propan-1-one] (ESACURE KIP, Fratelli Lamberti); Benzoin (2-Hydroxy-1,2-diphenylethanone) (ESACURE BO, Fratelli Lamberti); Benzoin ethyl ether (2-Ethoxy-1,2-diphenylethanone) (DAITOCURE EE, Siber Hegner); Benzoin isopropyl ether (2-Isopropoxy-1,2-diphenylethanone) (VICURE 30, Stauffer); Benzoin n-butyl ether (2-Butoxy-1,2-diphenylethanone) (ESACURE EB1, Fratelli Lamberti); mixture of benzoin butyl ethers (TRIGONAL 14, Akzo); Benzoin iso-butyl ether (2-Isobutoxy-1,2-diphenylethanone) (VICURE 10, Stauffer); blend of benzoin *n*-butyl ether and benzoin isobutyl ether (ESACURE

EB3, ESACURE EB4, Fratelli Lamberti); Benzildimethyl ketal (2,2-Dimethoxy-1,2-diphenylethanone) ("BDK") (IRGACURE 651, Ciba-Geigy); 2,2-Diethoxy-1,2-diphenylethanone (UVATONE 8302, Upjohn); α,α-Diethoxyacetophenone (2,2-Diethoxy-1-phenyl-ethanone) ("DEAP", Upjohn), (DEAP, Rahn); and α,α -Di-(*n*-butoxy)-acetophenone (2,2-Dibutoxyl-1-phenyl-ethanone) (UVATONE 8301, Upjohn).

It is known to those of ordinary skill in the art that the dehydration by conventional means of the tertiary alcohols that are alpha to the carbonyl groups is difficult. One conventional reaction that can be used to dehydrate the phthaloylglycine-2959 is by reacting the phthaloylglycine-2959 in anhydrous benzene in the presence of *p*-toluenesulfonic acid. After refluxing the mixture, the final product is isolated. However, the yield of the desired dehydrated alcohol is only about 15 to 20% by this method.

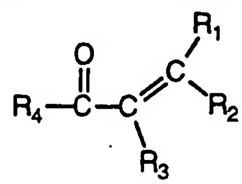
To increase the yield of the desired dehydrated phthaloylglycine-2959, a new reaction was invented. The reaction is summarized as follows:



It is to be understood that the groups on the carbon alpha to the carbonyl group can be groups other than methyl groups such as aryl or heterocyclic groups. The only limitation on these groups are steric limitations. Desirably, the metal salt used in the Nohr-MacDonald elimination reaction is $ZnCl_2$. It is to be understood that other transition metal salts can be used in performing the Nohr-MacDonald elimination reaction but $ZnCl_2$ is the preferred metal salt. The amount of metal salt used in the Nohr-MacDonald elimination reaction is desirably approximately equimolar to the tertiary alcohol compound, such as the

photoreactor. The concentration of tertiary alcohol in the reaction solution is between approximately 4% and 50% w/v.

Thus, the stabilizing composition produced by the process of dehydrating a tertiary alcohol that is alpha to a carbonyl group on a photoreactor is represented in the following general formula:



wherein R_1 is hydrogen, an alkane, an alkene, or an aryl group;

wherein R_2 is hydrogen, an alkane, an alkene, or an aryl group;

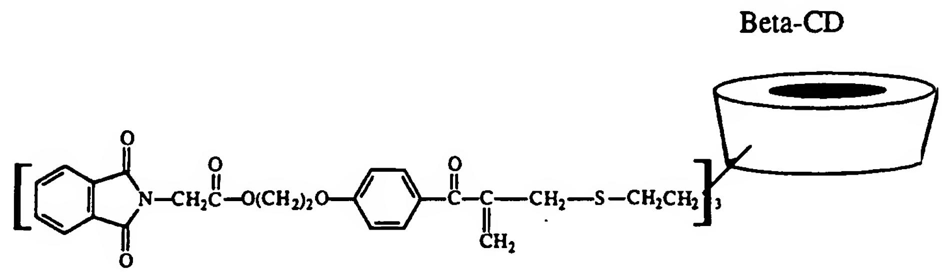
wherein R_3 is hydrogen, an alkane, an alkene, or an aryl group; and

wherein R_4 is an aryl, or substituted aryl group.

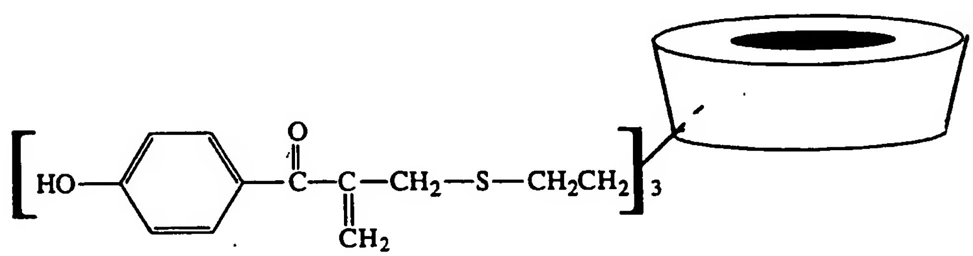
Another requirement of the reaction is that it be run in a non-aqueous, non-polar solvent. The preferred solvents for running the Nohr-MacDonald elimination reaction are aromatic hydrocarbons including, but not limited to, xylene, benzene, toluene, cumene, mesitylene, *p*-cymene, butylbenzene, styrene, and divinylbenzene. It is to be understood that other substituted aromatic hydrocarbons can be used as solvents in the present invention. *p*-Xylene is the preferred aromatic hydrocarbon solvent, but other isomers of xylene can be used in performing the Nohr-MacDonald elimination reaction.

An important requirement in performing the Nohr-MacDonald elimination reaction is that the reaction be run at a relatively high temperature. The reaction is desirably performed at a temperature of between approximately 80°C and 150°C. A suitable temperature for dehydrating phthaloylglycine-2959 is approximately 124°C. The time the reaction runs is not critical. The reaction should be run between approximately 30 minutes to 4 hours. However, depending upon the reactants and the solvent used, the timing may vary to achieve the desired yield of product.

It is to be understood that the dehydrated phthaloylglycine-2959 can be attached to the molecular includant in a variety of ways. In one embodiment, the dehydrated phthaloylglycine-2959 is covalently attached to the cyclodextrin as represented in the following formula:

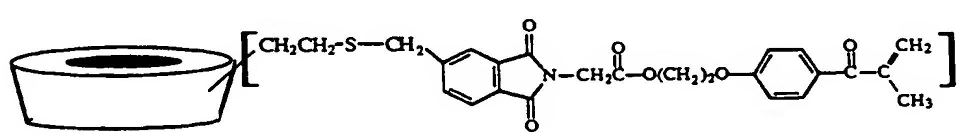


In another embodiment, as shown below, only the modified DARCUR 2959 without the phthaloyl glycine attached is reacted with the cyclodextrin to yield the following compound. This compound is capable of stabilizing a dye that is associated with the molecular includant and is represented by the following formula:



It is to be understood that photoreactors other than DARCUR 2959 can be used in the present invention.

In yet another embodiment, the dehydrated phthaloylglycine-2959 can be attached to the molecular includant via the opposite end of the molecule. One example of this embodiment is represented in the following formula:



As a practical matter, the colorant, ultraviolet radiation transorber, modified photoreactor, and molecular includant are likely to be solids depending upon the constituents used to prepare the molecules. However, any or all of such materials can be a liquid. The colored composition can be a liquid either because one or more of its components is a liquid, or, when the molecular includant is organic in nature, a solvent is employed. Suitable solvents include, but are not limited to, amides, such as N,N-dimethylformamide; sulfoxides, such as dimethylsulfoxide; ketones, such as acetone, methyl ethyl ketone, and methyl butyl ketone; aliphatic and aromatic hydrocarbons, such as hexane, octane, benzene, toluene, and the xylenes; esters, such as ethyl acetate; water; and the like. When the molecular includant is a cyclodextrin, particularly suitable solvents are the amides and sulfoxides.

In an embodiment where the composition of the present invention is a solid, the effectiveness of the above compounds on the colorant is improved when the colorant and the selected compounds are in intimate contact. To this end, the thorough blending of the components, along with other components which may be present, is desirable. Such blending generally is accomplished by any of the means known to those having ordinary skill in the art. When the colored composition includes a polymer, blending is facilitated if the colorant and the ultraviolet radiation transorber are at least partly soluble in softened or molten polymer. In such case, the composition is readily prepared in, for example, a two-roll mill. Alternatively, the composition of the present invention can be a liquid because one or more of its components is a liquid.

For some applications, the composition of the present invention typically will be utilized in particulate form. In other applications, the particles of the composition should be very small. Methods of forming such particles are well known to those having ordinary skill in the art.

The colored composition of the present invention can be utilized on or in any substrate. If one desires to mutate the colored composition that is present in a substrate, however, the substrate should be substantially transparent to the ultraviolet radiation which is employed to mutate the colorant. That is, the ultraviolet radiation will not significantly interact with or be absorbed by the substrate. As a practical matter, the composition typically will be placed on a substrate, with the most common substrate being paper. Other substrates, including, but not limited to, woven and nonwoven webs or fabrics, films, and the like, can be used, however.

The colored composition optionally may also contain a carrier, the nature of which is well known to those having ordinary skill in the art. For many applications, the carrier will be a polymer, typically a thermosetting or thermoplastic polymer, with the latter being the more common.

Further examples of thermoplastic polymers include, but are not limited to: end-capped polyacetals, such as poly(oxymethylene) or polyformaldehyde, poly(trichloroacetaldehyde), poly(n-valeraldehyde), poly(acetaldehyde), poly(propionaldehyde), and the like; acrylic polymers, such as polyacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), poly(methyl methacrylate), and the like; fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylenepropylene copolymers, ethylenetetrafluoroethylene copolymers, poly-(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), poly(vinyl fluoride), and the like; epoxy resins, such as the condensation products of epichlorohydrin and bisphenol A; polyamides, such as poly(6-aminocaproic acid) or poly(E-caprolactam), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(11-aminoundecanoic acid), and the like; polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloyl) or poly(m-phenylene isophthalamide), and the like; parylenes, such as poly-*p*-xylylene,

poly(chloro-*p*-xylene), and the like; polyaryl ethers, such as poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(*p*-phenylene oxide), and the like; polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene), poly(sulfonyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-4,4-biphenylene), and the like; polycarbonates, such as poly(bisphenol A) or poly(carbonyldioxy-1,4-phenyleneisopropylidene-1,4-phenylene), and the like; polyesters, such as poly(ethylene terephthalate), poly(tetramethylene terephthalate), poly(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexylenemethyleneoxyterephthaloyl), and the like; polyaryl sulfides, such as poly(*p*-phenylene sulfide) or poly(thio-1,4-phenylene), and the like; polyimides, such as poly-(pyromellitimido-1,4-phenylene), and the like; polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, polychloroprene, polyacrylonitrile, poly(vinyl acetate), poly(vinylidene chloride), polystyrene, and the like; and copolymers of the foregoing, such as acrylonitrile-butadienestyrene (ABS) copolymers, styrene-n-butylmethacrylate copolymers, ethylene-vinyl acetate copolymers, and the like.

Some of the more commonly used thermoplastic polymers include styrene-n-butyl methacrylate copolymers, polystyrene, styrene-n-butyl acrylate copolymers, styrene-butadiene copolymers, polycarbonates, poly(methyl methacrylate), poly(vinylidene fluoride), polyamides (nylon-12), polyethylene, polypropylene, ethylene-vinyl acetate copolymers, and epoxy resins.

Examples of thermosetting polymers include, but are not limited to, alkyd resins, such as phthalic anhydride-glycerol resins, maleic acid-glycerol resins, adipic acid-glycerol resins, and phthalic anhydride-pentaerythritol resins; allylic resins, in which such monomers as diallyl phthalate, diallyl isophthalate

diallyl maleate, and diallyl chlorendate serve as nonvolatile cross-linking agents in polyester compounds; amino resins, such as aniline-formaldehyde resins, ethylene urea-formaldehyde resins, dicyandiamide-formaldehyde resins, melamine-formaldehyde resins, sulfonamide-formaldehyde resins, and urea-formaldehyde resins; epoxy resins, such as cross-linked epichlorohydrin-bisphenol A resins; phenolic resins, such as phenol-formaldehyde resins, including Novolacs and resols; and thermosetting polyesters, silicones, and urethanes.

In addition to the colorant, and ultraviolet radiation transorber or functionalized molecular includant, modified photoreactor, and optional carrier, the colored composition of the present invention also can contain additional components, depending upon the application for which it is intended. Examples of such additional components include, but are not limited to, charge carriers, stabilizers against thermal oxidation, viscoelastic properties modifiers, cross-linking agents, plasticizers, charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; and fillers such as calcium carbonate, clay and talc, among other additives used by those having ordinary skill in the art. Charge carriers are well known to those having ordinary skill in the art and typically are polymer-coated metal particles. The identities and amounts of such additional components in the colored composition are well known to one of ordinary skill in the art.

The present invention comprises a substrate, such as an optical disk, having a layer of the colored composition disposed thereon to form a recording layer. Briefly described, the method of recording information on the recording layer comprises selectively irradiating regions of the recording layer comprising a composition containing a mutable colorant and a radiation transorber, particularly an ultraviolet radiation transorber, with radiation, particularly ultraviolet radiation, at a dosage level

sufficient to mutate the colorant. As stated above, in one embodiment the composition which forms the recording layer further includes a molecular includant.

As stated above, the amount or dosage level of radiation that the colorant of the present invention is exposed to will generally be that amount which is necessary to mutate the colorant. The amount of radiation necessary to mutate the colorant can be determined by one of ordinary skill in the art using routine experimentation. Power density is the measure of the amount of radiated electromagnetic power traversing a unit area and is usually expressed in watts per centimeter squared (W/cm^2). The power density level range is between approximately 5 mW/cm^2 and 15 mW/cm^2, more particularly 8 to 10 mW/cm^2.

The colored composition of the present invention can be utilized in a recording medium, such as on the substrate 12 of the optical disk 10 shown in Fig. 7, to thereby form a recording layer, such as the recording layer 14 on one side of the optical disk. It is preferred that the colored composition be combined with a polymer, such as a thermoforming or thermosetting plastic polymer, before it is applied to the substrate 12. The polymer provides a matrix within which to contain the colored composition, to bind the colored composition to the recording medium substrate 12 and to protect the colored composition from damage, such as by wear, abrasion, dirt and the like. The polymer containing the colored composition can be applied to the substrate 12 by conventional techniques, such as spin coating, roll coating, spraying and the like, in order to form a relatively thin layer on the surface of the substrate. This thin layer of colored composition and polymer forms the recording layer 14 of the optical disk 10. The techniques for forming a polymer recording layer on a recording medium substrate are well known to those skilled in the art and can be utilized in the present invention.

If the composition is combined with a polymer, the polymer should be substantially transparent to the mutating

ultraviolet radiation which is employed to mutate the colorant. That is, the ultraviolet radiation should not significantly interact with or be absorbed by the polymer. Suitable polymers for use when the mutating radiation is ultraviolet light include, but are not limited to, those polymers listed above.

Alternately, the colored composition can be incorporated with the material from which the recording medium substrate 12 is formed, again provided that the material is substantially transparent to the mutating radiation (Fig. 9). Therefore, the colored composition can be combined with a suitable polymer and then molded or otherwise formed into the recording medium, such as a disk, either plastic or metal, a film, a tape or the like. It is particularly preferred that the colored composition and polymer be formed into a plastic disk, such as an optical disk; especially a compact disc. The techniques for forming polymers into disks, films, tapes or the like, are well known to those skilled in the art and can be utilized in the present invention.

This alternate embodiment is illustrated in Fig. 9. Instead of having a recording layer formed on one surface of the recording medium substrate 12, the substrate itself becomes the recording layer. By eliminating the need for forming a thin layer on the surface of the substrate, a complex manufacturing task can be eliminated, thereby making the recording medium easier to produce.

The optical disk 10 (Fig. 7) can be "recorded" with digital information, such as music, video, computer data, computer software, etc., by selectively exposing the recording layer 14 to mutating light, particularly ultraviolet light. The optical disk 10 is placed in a suitable optical disk drive (not shown) so that the disk is rotatably driven. Referring now to Fig. 8, positioned above the surface of the disk 10 which includes the recording layer 14 is an excimer laser 16 which emits controlled pulses of ultraviolet light 18 of a wavelength suitable to mutate the colorant in the recording layer. When the ultraviolet light 18 strikes the recording layer, it causes the colorant to mutate only in that area

which is irradiated. Since the disk 10 is rotated and since the ultraviolet light 18 is pulsed, the portion of the recording layer 14 which is exposed to the radiation is a small arc 20. This small arcuate area 20 changes color from that of its surrounding area 22. The colorant in the colored composition is selected so that the color change produces the maximum contrast between the area of mutated color and the area of nonmutated color. The excimer laser 16 is controlled by a computer (not shown) so that the pulses of light emitted by the laser correspond to encoded information which is to be recorded on the disk. The series of pulses of light from the laser 16 produce a series of mutated arcuate areas formed in a track around the disk 10 (Fig. 10). The excimer laser 16 is radially movable with respect to the disk, as shown by the arrow "A," so that multiple tracks can be recorded on the disk. Each area of mutated colorant corresponds to one portion of a binary signal. For example, as shown in Fig. 10, the longer arcualte arcs 20a correspond to the binary digit "1" and the shorter arcuate arcs 20b correspond to the binary digit "0." In this manner, a series of on's and off's, pluses and minuses, yeses and nos and the like, can be recorded on the recording layer 14. This binary information corresponds to encoded information in a digitally encoded format.

Alternately, for mass production of optical disk in accordance with the present invention, the optical disk 10 (Fig. 11) can be "recorded" with digital information by selectively exposing the recording layer 14 to ultraviolet light by placing a mask 24 over the recording layer and exposing the mask and underlying recording layer to ultraviolet light 26 from an excimer lamp 28. The mask 24 includes portions 30 which are transparent to ultraviolet radiation and portions 32 which are opaque to ultraviolet radiation. Typically, the mask 24 will be made by photographic processes, or other similar processes, well known to those skilled in the art. Furthermore, the transparent portions 30 of the mask 24 correspond to the arcuate portions 20 on the disc 10. When the ultraviolet light 26 irradiates the mask

24, the ultraviolet light passes through the mask at the transparent portions 30 thereby selectively exposing the recording layer 14 to ultraviolet radiation at the portions 20, thereby mutating the colorant at those locations. The mask 24 blocks or absorbs the ultraviolet radiation at locations other than the transparent portions 30 so that the areas surrounding the portions 20 remain unmutated. When the mask 24 is removed from the disc 10, the recording layer 14 will in effect contain a photographic image of the pattern of transparent portions of the mask. Although the recording process utilizing the mask is different from the process utilizing an excimer laser, the resulting disc 10 is identical in all essential aspects.

Referring now to Figure 9, it is to be understood that the above methods of producing and recording optical disks in accordance with the present invention also apply towards producing and recording optical disks where the substrate itself is the recording layer.

Referring again to Figure 8, the binary digital information contained in the recording layer 14 can be "read" from the disc 10 by illuminating the recording track with nonmutating radiation, such as visible light 34 from a conventional red laser 36. Since the light from the laser 36 is of a wavelength to which the colorant in the recording layer is stable, the color of the colorant, whether already mutated or not, will be unchanged by the laser light 34. Since the mutated arcuate portions, such as 20, of the recording layer 14 have a different color, and, therefore, a different reflectance than the unmutated portions, the light which is reflected from the recording layer 14 varies in intensity corresponding to the pattern of mutated arcuate portions 20 on the disc 10. The varying intensity of the reflected light 38 is detected by a photodetector 40 which produces and electrical signal corresponding to the varying intensity of the reflected light. The electrical signal from the photodetector 40 is sent to a computer where it is digitized stored or otherwise processed for its intended use.

Referring now to Figure 9, it is to be understood that the above method of reading optical disks in accordance with the present invention also apply towards reading optical disks where the substrate itself is the recording layer. Accordingly, the same methods of recording and reading optical disks may be used whether the mutable colorant of the present invention is present as a layer 14 on the substrate 12 (Fig. 8), or whether the mutable colorant is in the substrate 12 (Fig. 9).

It will be appreciated that since the colorant in the recording layer is color-stable with respect to sunlight and artificial light, light from those sources, such as at 42, will not mutate the colorant, and, thereby, does not cause fading of the colorant. This results in a relatively permanent recording medium which is stable with respect to most conventional environmental conditions.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or scope of the present invention. In the examples, all parts are parts by weight unless stated otherwise.

EXAMPLE 1

This example describes the preparation of a β-cyclodextrin molecular includant having (1) an ultraviolet radiation transorber covalently bonded to the cyclodextrin outside of the cavity of the cyclodextrin, and (2) a colorant associated with the cyclodextrin by means of hydrogen bonds and/or van der Waals forces.

A. Friedel-Crafts Acylation of Transorber

A 250-ml, three-necked, round-bottomed reaction flask was fitted with a condenser and a pressure-equalizing addition funnel equipped with a nitrogen inlet tube. A magnetic stirring bar was placed in the flask. While being flushed with nitrogen, the flask was charged with 10 g (0.05 mole) of 1-hydroxycyclohexyl phenyl ketone (IRGACURE 184, Ciba-Geigy Corporation,

Hawthorne, New York), 100 ml of anhydrous tetrahydofuran (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), and 5 g (0.05 mole) of succinic anhydride (Aldrich Chemical Co., Milwaukee, WI). To the continuously stirred contents of the flask then was added 6.7 g of anhydrous aluminum chloride (Aldrich Chemical Co., Milwaukee, Wisconsin). The resulting reaction mixture was maintained at about 0°C in an ice bath for about one hour, after which the mixture was allowed to warm to ambient temperature for two hours. The reaction mixture then was poured into a mixture of 500 ml of ice water and 100 ml of diethyl ether. The ether layer was removed after the addition of a small amount of sodium chloride to the aqueous phase to aid phase separation. The ether layer was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving 12.7 g (87 percent) of a white crystalline powder. The material was shown to be 1-hydroxycyclohexyl 4-(2-carboxyethyl)carbonylphenyl ketone by nuclear magnetic resonance analysis.

B. Preparation of Acylated Transorber Acid Chloride

A 250-ml round-bottomed flask fitted with a condenser was charged with 12.0 g of 1-hydroxycyclohexyl 4-(2-carboxyethyl)carbonylphenyl ketone (0.04 mole), 5.95 g (0.05 mole) of thionyl chloride (Aldrich Chemical Co., Milwaukee, Wisconsin), and 50 ml of diethyl ether. The resulting reaction mixture was stirred at 30°C for 30 minutes, after which time the solvent was removed under reduced pressure. The residue, a white solid, was maintained at 0.01 Torr for 30 minutes to remove residual solvent and excess thionyl chloride, leaving 12.1 g (94 percent) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone.

C. Covalent Bonding of Acylated Transorber to Cyclodextrin

A 250-ml, three-necked, round-bottomed reaction flask containing a magnetic stirring bar and fitted with a thermometer,

condenser, and pressure-equalizing addition funnel equipped with a nitrogen inlet tube was charged with 10 g (9.8 mmole) of ß-cyclodextrin (American Maize-Products Company, Hammond, Indiana), 31.6 g (98 mmoles) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone, and 100 ml of N,N-dimethylformamide while being continuously flushed with nitrogen. The reaction mixture was heated to 50°C and 0.5 ml of triethylamine added. The reaction mixture was maintained at 50°C for an hour and allowed to cool to ambient temperature. In this preparation, no attempt was made to isolate the product, a ß-cyclodextrin to which an ultraviolet radiation transorber had been covalently coupled (referred to hereinafter for convenience as ß-cyclodextrin-transorber).

The foregoing procedure was repeated to isolate the product of the reaction. At the conclusion of the procedure as described, the reaction mixture was concentrated in a rotary evaporator to roughly 10 percent of the original volume. The residue was poured into ice water to which sodium chloride then was added to force the product out of solution. The resulting precipitate was isolated by filtration and washed with diethyl ether. The solid was dried under reduced pressure to give 24.8 g of a white powder. In a third preparation, the residue remaining in the rotary evaporator was placed on top of an approximately 7.5-cm column containing about 15 g of silica gel. The residue was eluted with N,N-dimethylformamide, with the eluant being monitored by means of Whatman® Flexible-Backed TLC Plates (Catalog No. 05-713-161, Fisher Scientific, Pittsburgh, Pennsylvania). The eluted product was isolated by evaporating the solvent. The structure of the product was verified by nuclear magnetic resonance analysis.

D. Association of Colorant with Cyclodextrin-Transorber-Preparation of Colored Composition

To a solution of 10 g (estimated to be about 3.6 mmole) of β–cyclodextrin-transorber in 150 ml of N,N-dimethylformamide

in a 250-ml round-bottomed flask was added at ambient temperature 1.2 g (3.6 mmole) of Malachite Green oxalate (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), referred to hereinafter as Colorant A for convenience. The reaction mixture was stirred with a magnetic stirring bar for one hour at ambient temperature. Most of the solvent then was removed in a rotary evaporator and the residue was eluted from a silica gel column as already described. The beta-cyclodextrin-transorber Colorant A inclusion complex moved down the column first, cleanly separating from both free Colorant A and beta-cyclodextrin-transorber. The eluant containing the complex was collected and the solvent removed in a rotary evaporator. The residue was subjected to a reduced pressure of 0.01 Torr to remove residual solvent to yield a blue-green powder.

E. Mutation of Colored Composition

The beta-cyclodextrin-transorber Colorant A inclusion complex was exposed to ultraviolet radiation from two different lamps, Lamps A and B. Lamp A was a 222-nanometer excimer lamp assembly organized in banks of four cylindrical lamps having a length of about 30 cm. The lamps were cooled by circulating water through a centrally located or inner tube of the lamp and, as a consequence, they operated at a relatively low temperature, *i.e.*, about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m^2). However, such range in reality merely reflects the capabilities of current excimer lamp power supplies; in the future, higher power densities may be practical. The distance from the lamp to the sample being irradiated was 4.5 cm. Lamp B was a 500-watt Hanovia medium pressure mercury lamp (Hanovia Lamp Co., Newark, New Jersey). The distance from Lamp B to the sample being irradiated was about 15 cm.

A few drops of an N,N-dimethylformamide solution of the beta-cyclodextrin-transorber Colorant A inclusion complex were placed on a TLC plate and in a small polyethylene weighing pan.

Both samples were exposed to Lamp A and were decolorized (mutated to a colorless state) in 15-20 seconds. Similar results were obtained with Lamp B in 30 seconds.

A first control sample consisting of a solution of Colorant A and beta-cyclodextrin in N,N-dimethylformamide was not decolorized by Lamp A. A second control sample consisting of Colorant A and 1-hydroxycyclohexyl phenyl ketone in N,N-dimethylformamide was decolorized by Lamp A within 60 seconds. On standing, however, the color began to reappear within an hour.

To evaluate the effect of solvent on decolorization, 50 mg of the beta-cyclodextrin-transorber Colorant A inclusion complex was dissolved in 1 ml of solvent. The resulting solution or mixture was placed on a glass microscope slide and exposed to Lamp A for 1 minute. The rate of decolorization, i.e., the time to render the sample colorless, was directly proportional to the solubility of the complex in the solvent, as summarized below.

Table 1

Solvent	Solubility	Decolorization Time
N,N-Dimethylformamide	Poor	1 minute
Dimethylsulfoxide	Soluble	<10 seconds
Acetone	Soluble	<10 seconds
Hexane	Insoluble	--
Ethyl Acetate	Poor	1 minute

Finally, 10 mg of the beta-cyclodextrin-transorber Colorant A inclusion complex were placed on a glass microscope slide and crushed with a pestle. The resulting powder was exposed to Lamp A for 10 seconds. The powder turned colorless. Similar results were obtained with Lamp B, but at a slower rate.

EXAMPLE 2

Because of the possibility in the preparation of the colored composition described in the following examples for the acylated transorber acid chloride to at least partially occupy the cavity of the cyclodextrin, to the partial or complete exclusion of colorant, a modified preparative procedure was carried out. Thus, this example describes the preparation of a beta-cyclodextrin molecular includant having (1) a colorant at least partially included within the cavity of the cyclodextrin and associated therewith by means of hydrogen bonds and/or van der Waals forces, and (2) an ultraviolet radiation transorber covalently bonded to the cyclodextrin substantially outside of the cavity of the cyclodextrin.

A. *Association of Colorant with a Cyclodextrin*

To a solution of 10.0 g (9.8 mmole) of beta-cyclodextrin in 150 ml of N,N-dimethylformamide was added 3.24 g (9.6 mmoles) of Colorant A. The resulting solution was stirred at ambient temperature for one hour. The reaction solution was concentrated under reduced pressure in a rotary evaporator to a volume about one-tenth of the original volume. The residue was passed over a silica gel column as described in Part C of Example 1. The solvent in the eluant was removed under reduced pressure in a rotary evaporator to give 12.4 g of a blue-green powder, beta-cyclodextrin Colorant A inclusion complex.

B. *Covalent Bonding of Acylated Transorber to Cyclodextrin Colorant Inclusion Complex - Preparation of Colored Composition*

A 250-ml, three-necked, round-bottomed reaction flask containing a magnetic stirring bar and fitted with a thermometer, condenser, and pressure-equalizing addition funnel equipped with a nitrogen inlet tube was charged with 10 g (9.6 mmole) of beta-cyclodextrin Colorant A inclusion complex, 31.6 g (98 mmoles) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone prepared as described in Part B of Example 1, and 150 ml

of N,N-dimethylformamide while being continuously flushed with nitrogen. The reaction mixture was heated to 50°C and 0.5 ml of triethylamine added. The reaction mixture was maintained at 50°C for an hour and allowed to cool to ambient temperature. The reaction mixture then was worked up as described in Part A, above, to give 14.2 g of beta-cyclodextrin-transorber Colorant A inclusion complex, a blue-green powder.

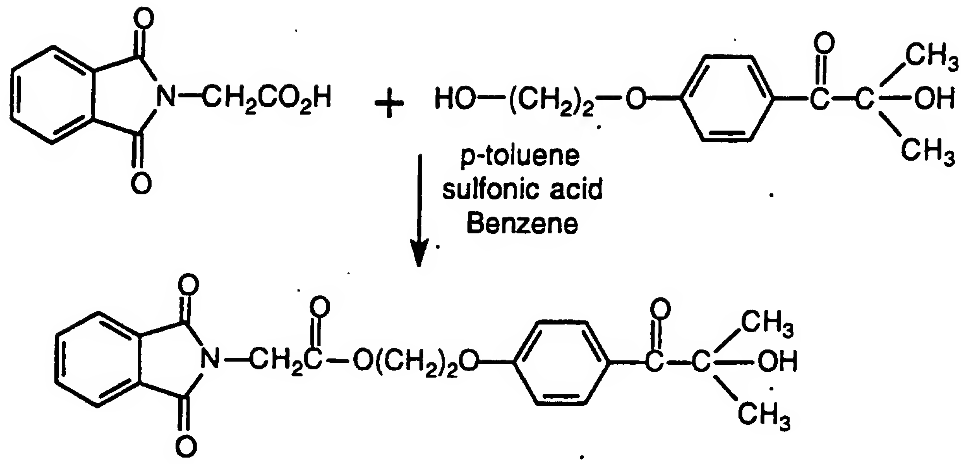
C. Mutation of Colored Composition

The procedures described in Part E of Example 1 were repeated with the beta-cyclodextrin-transorber Colorant A inclusion complex prepared in Part B, above, with essentially the same results.

EXAMPLE 3

This example describes a method of preparing an ultraviolet radiation transorber, 2-[*p*-(2-methyllactoyl)phenoxy]ethyl 1,3-dioxo-2-isoindolineacetate, designated phthaloylglycine-2959.

The following was admixed in a 250 ml, three-necked, round bottomed flask fitted with a Dean & Stark adapter with condenser and two glass stoppers: 20.5g (0.1 mole) of the wavelength selective sensitizer, phthaloylglycine (Aldrich Chemical Co., Milwaukee, Wisconsin); 24.6 g (0.1mole) of the photoreactor, DARCUR 2959 (Ciba-Geigy, Hawthorne, New York); 100 ml of benzene (Aldrich Chemical Co., Milwaukee, Wisconsin); and 0.4 g *p*-toluenesulfonic acid (Aldrich Chemical Co., Milwaukee, Wisconsin). The mixture was heated at reflux for 3 hours after which time 1.8 ml of water was collected. The solvent was removed under reduced pressure to give 43.1 g of white powder. The powder was recrystallized from 30% ethyl acetate in hexane (Fisher) to yield 40.2 g (93%) of a white crystalline powder having a melting point of 153-4°C. The reaction is summarized as follows:



The resulting product, designated phthaloylglycine-2959, had the following physical parameters:

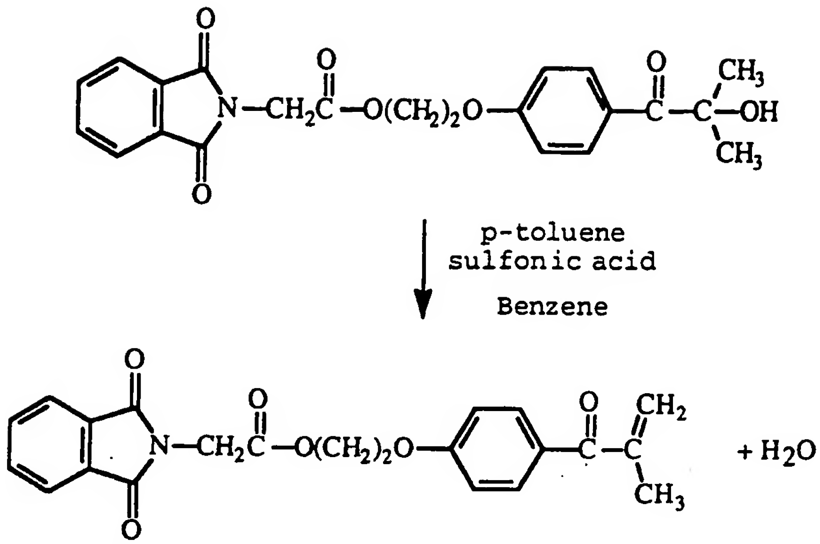
IR [NUJOL MULL] ν_{max} 3440, 1760, 1740, 1680, 1600 cm-1

1H NMR [CDCl3] ∂ppm 1.64[s], 4.25[m], 4.49[m], 6.92[m], 7.25[m], 7.86[m], 7.98[m], 8.06[m] ppm

Example 4

This example describes a method of dehydrating the phthaloylglycine-2959 produced in Example 3.

The following was admixed in a 250 ml round bottomed flask fitted with a Dean & Stark adapter with condenser: 21.6 g (0.05 mole) phthaloylglycine-2959; 100 ml of anhydrous benzene (Aldrich Chemical Co., Milwaukee, Wisconsin); and 0.1 g *p*-toluenesulfonic acid (Aldrich Chemical Co., Milwaukee, Wisconsin). The mixture was refluxed for 3 hours. After 0.7 ml of water had been collected in the trap, the solution was then removed under vacuum to yield 20.1 g (97%) of a white solid. However, analysis of the white solid showed that this reaction yielded only 15 to 20% of the desired dehydration product. The reaction is summarized as follows:



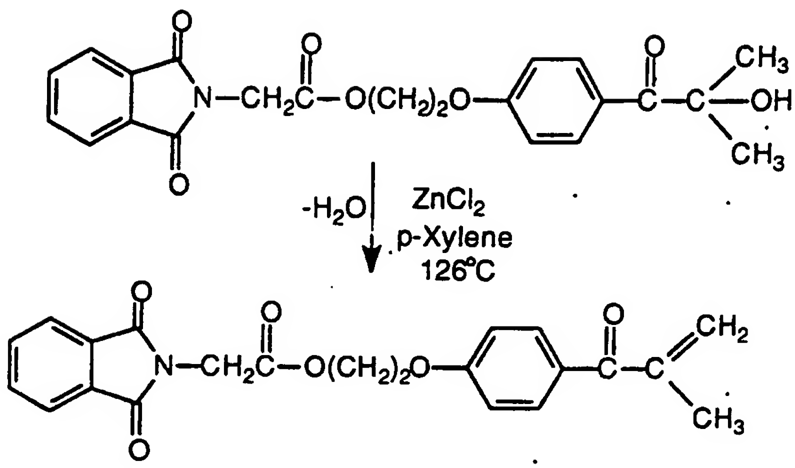
The resulting reaction product had the following physical parameters:

IR (NUJOL) ν_{max} 1617cm-1 (C=C-C=O)

Example 5

This example describes the Nohr-MacDonald elimination reaction used to dehydrate the phthaloylglycine-2959 produced in Example 3.

Into a 500 ml round bottomed flask were placed a stirring magnet, 20.0g (0.048 mole) of the phthaloylglycine-2959, and 6.6 g (0.048 mole) of anhydrous zinc chloride (Aldrich Chemical Co., Milwaukee, Wisconsin). 250 ml of anhydrous *p*-xylene (Aldrich Chemical Co., Milwaukee, Wisconsin) was added and the mixture refluxed under argon atmosphere for two hours. The reaction mixture was then cooled, resulting in a white precipitate which was collected. The white powder was then recrystallized from 20% ethyl acetate in hexane to yield 18.1 g (95%) of a white powder. The reaction is summarized as follows:



The resulting reaction product had the following physical parameters:

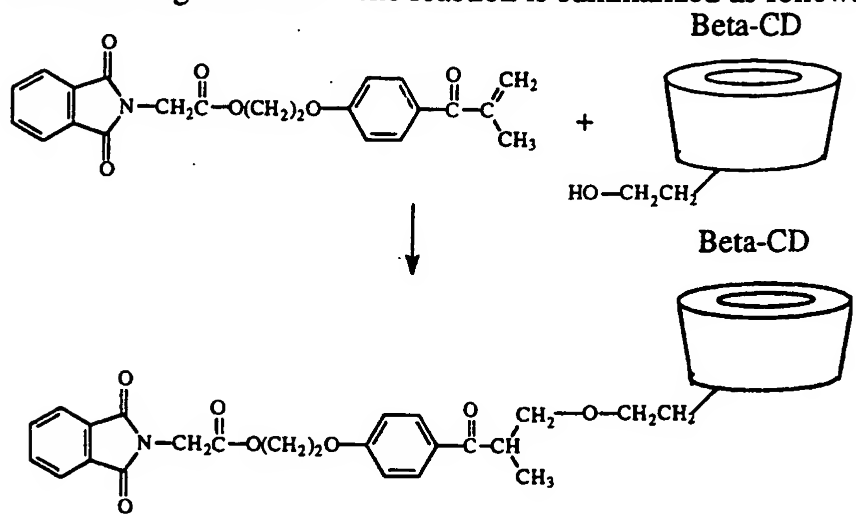
Melting Point: 138°C to 140°C.
Mass spectrum: m/e: 393 M +, 352, 326, 232, 160.
IR (KB) ν_{max} 1758, 1708, 1677, 1600 cm-1
1H NMR [DMSO] ∂ppm 1.8(s), 2.6(s), 2.8 (d), 3.8 (d), 4.6 (m), 4.8 (m), 7.3(m), 7.4 (m), 8.3 (m), and 8.6 (d)
13C NMR [DMSO] ∂ppm 65.9 (CH2=)

Example 6

This example describes a method of producing a beta-cyclodextrin having dehydrated phthaloylglycine-2959 groups from Example 4 or 5 covalently bonded thereto.

The following was admixed in a 100 ml round-bottomed flask: 5.0 g (4 mmole) beta-cyclodextrin (American Maize Product Company, Hammond, Indiana) (designated beta-CD in the following reaction); 8.3 g (20 mmole) dehydrated phthaloylglycine-2959; 50 ml of anhydrous DMF; 20 ml of benzene; and 0.01 g *p*-tolulenesulfonyl chloride (Aldrich Chemical Co., Milwaukee, Wisconsin). The mixture was chilled in a salt/ice bath and stirred for 24 hours. The reaction mixture was poured into 150 ml of weak sodium bicarbonate solution and

extracted three times with 50 ml ethyl ether. The aqueous layer was then filtered to yield a white solid comprising the beta-cyclodextrin with phthaloylglycine-2959 group attached. A yield of 9.4 g was obtained. Reverse phase TLC plate using a 50:50 DMF:acetonitrile mixture showed a new product peak compared to the starting materials. The reaction is summarized as follows:



The beta-cyclodextrin molecule has several primary alcohols and secondary alcohols with which the phthaloylglycine-2959 can react. The above representative reaction only shows a single phthaloylglycine-2959 molecule for illustrative purposes.

Example 7

This example describes a method of associating a colorant and an ultraviolet radiation transorber with a molecular includant. More particularly, this example describes a method of associating the colorant crystal violet with the molecular includant beta-cyclodextrin covalently bonded to the ultraviolet radiation transorber dehydrated phthaloylglycine-2959 of Example 6.

The following was placed in a 100 ml beaker: 4.0 g beta-cyclodextrin having a dehydrated phthaloylglycine-2959 group; and 50 ml of water. The water was heated to 70°C at which point the solution became clear. Next, 0.9 g (2.4 mmole) crystal violet

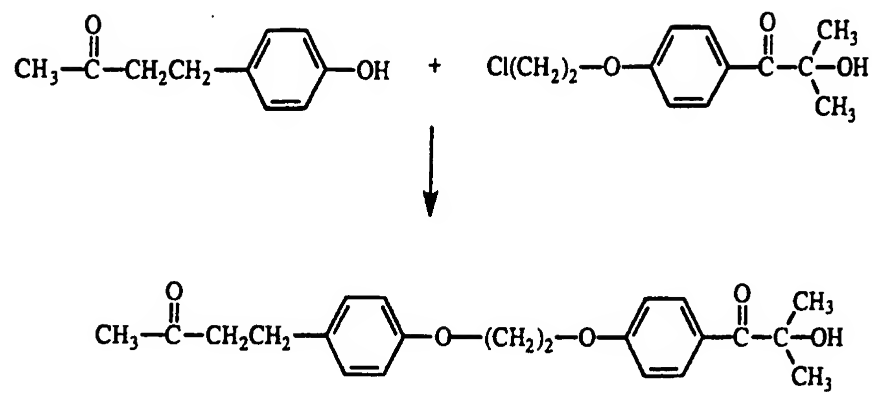
(Aldrich Chemical Company, Milwaukee, Wisconsin) was added to the solution, and the solution was stirred for 20 minutes. Next, the solution was then filtered. The filtrand was washed with the filtrate and then dried in a vacuum oven at 84°C. A violet-blue powder was obtained having 4.1 g (92%) yield. The resulting reaction product had the following physical parameters:

U.V. Spectrum DMF ν_{max} 610 nm (cf cv ν_{max} 604 nm)

Example 8

This example describes a method of producing the ultraviolet radiation transorber 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted).

The following was admixed in a 250 ml round-bottomed flask fitted with a condenser and magnetic stir bar: 17.6 g (0.1mole) of the wavelength selective sensitizer, 4(4-hydroxyphenyl) butan-2-one (Aldrich Chemical Company, Milwaukee, Wisconsin); 26.4 g (0.1 mole) of the photoreactor, chloro substituted DARCUR 2959 (Ciba-Geigy Corporation, Hawthorne, New York); 1.0 ml of pyridine (Aldrich Chemical Company, Milwaukee, Wisconsin); and 100 ml of anhydrous tetrahydrofuran (Aldrich Chemical Company, Milwaukee, Wisconsin). The mixture was refluxed for 3 hours and the solvent partially removed under reduced pressure (60% taken off). The reaction mixture was then poured into ice water and extracted with two 50 ml aliquots of diethyl ether. After drying over anhydrous magnesium sulfate and removal of solvent, 39.1 g of white solvent remained. Recrystallization of the powder from 30% ethyl acetate in hexane gave 36.7 g (91%) of a white crystalline powder, having a melting point of 142-3°C. The reaction is summarized in the following reaction:



The resulting reaction product had the following physical parameters:

IR [NUJOL MULL] ν_{max} 3460, 1760, 1700, 1620, 1600 cm-1

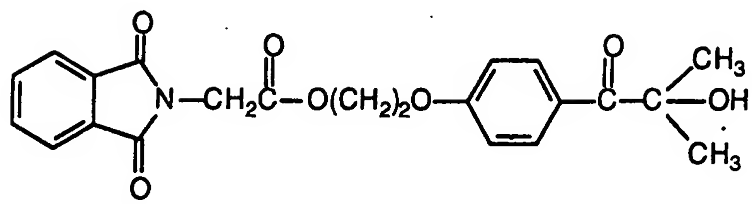
1H [CDCl3] ∂ppm 1.62[s], 4.2[m], 4.5[m], 6.9[m] ppm

The ultraviolet radiation transorber produced in this example, 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted), may be associated with beta-cyclodextrin and a colorant such as crystal violet, using the methods described above wherein 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted) would be substituted for the dehydrated phthaloylglycine-2959.

Example 9

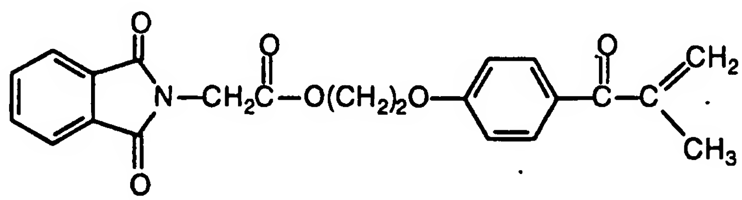
Stabilizing activity of the radiation transorber

This example demonstrates the ability of the present invention to stabilize colorants against light. Victoria Pure Blue BO is admixed in acetonitrile with phthaloylglycine-2959. The compounds are summarized by the following formulas:



phthaloylglycine-2959

and dehydrated phthaloylglycine-2959:



Solutions were prepared according to Table 2. The dye solutions were carefully, uniformly spread on steel plates to a thickness of approximately 0.1 mm. The plates were then immediately exposed to a medium pressure 1200 watt high intensity quartz arc mercury discharge lamp (Conrad-Hanovia, Inc., Newark, New Jersey) at a distance of 30 cm from the light. The mercury discharge light is a source of high intensity, broad spectrum light that is used in accelerated fading analyses. Table 2 shows the results of the fade time with the various solutions. Fade time is defined as the time until the dye became colorless to the naked eye.

Table 2

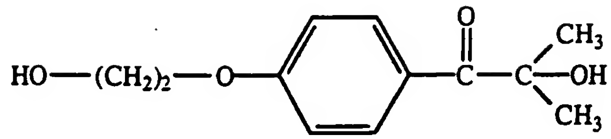
Phthaloylglycine-2959	Victoria pure Blue BO	Fade Time
3 parts by weight	1 part by weight	2 min
10 parts by weight	1 part by weight	1 1/2 min
20 parts by weight	1 part by weight	30 sec

Dehydrated Phthaloylglycine-2959	Victoria pure Blue BO	Fade Time
3 parts by weight	1 part by weight	4 min
10 parts by weight	1 part by weight	8 min
20 parts by weight	1 part by weight	>10 min

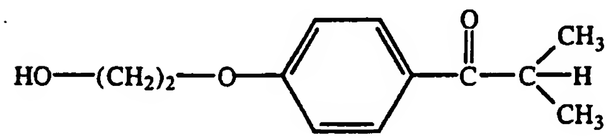
As can be seen in Table 2, when phthaloylglycine-2959 was admixed with Victoria Pure Blue BO, the dye faded when exposed to the mercury dwascharge light. However, when dehydrated phthaloylglycine-2959 was admixed with the Victoria Pure Blue BO at a ratio of 10 parts dehydrated phthaloylglycine-2959 to one part Victoria Pure Blue BO, there was increased stabilization of the dye to light. When the ratio was 20 parts dehydrated phthaloylglycine-2959 to one part Victoria Pure Blue BO, the dye was substantially stabilized to the mercury dwascharge light in the time limits of the exposure.

Example 10

To determine whether the hydroxy and the dehydroxy 2959 have the capability to stabilize colorants the following experiment was conducted. The compounds represented by the following formulas were tested as described below:



2959



Dehydroxy 2959

20 parts by weight of the hydroxy and the dehydroxy 2959 were admixed separately to one part by weight of Victoria Pure Blue BO in acetonitrile. The dye solutions were cwerefully uniformly spread on steel plates to a thickness of approximately 0.1 mm. The plates were then immediately exposed to a mercury discharge light at a distance of 30 cm from the light. The mercury discharge light is a source of high intensity, broad spectrum light that is used in accelerated fading analyses. Table 3 shows the results of the fade time with the various solutions. Fade time is defined as the time until the dye became colorless to the naked eye.

Table 3

Compound	Victoria Blue	Fade Time
20 parts 2959 (Hydroxy)	1 part	< 2 min
20 parts 2959 (Dehydroxy)	1 part	< 2 min
None	1 part	< 2 min

Example 11

Stabilizing activity of the radiation transorber and a molecular includant

This example demonstrates the capability of dehydrated phthaloylglycine-2959 bound to beta-cyclodextrin to stabilize dyes against light. The Victoria Pure Blue BO associated with the

radiation transorber, as discussed in the examples above, was tested to determine its capability to stabilize the associated dye against light emitted from a mercury discharge light. In addition, the Victoria Pure Blue BO alone and Victoria Pure Blue BO admixed with beta cyclodextrin were tested as controls. The compositions tested were as follows:

1. Victoria Pure Blue BO only at a concentration of 10mg/ml in acetonitrile.

2. Victoria Pure Blue BO included in beta cyclodextrin at a concentration of 20 mg/ml in acetonitrile.

3. The Victoria Pure Blue BO included in beta cyclodextrin to which the radiation transorber (dehydrated phthaloylglycine-2959) is covalently attached at a concentration of 20 mg/ml in acetonitrile.

The protocol for testing the stabilizing qualities of the three compositions is as follows: the dye solutions were carefully, uniformly spread on steel plates to a thickness of approximately 0.1 mm. The plates were then immediately exposed to a medium pressure 1200 watt high intensity quartz arc mercury discharge lamp (Conrad-Hanovia, Inc., Newark, New Jersey) at a distance of 30 cm from the lamp.

Table 4

Composition	Fade Time
1	5 sec
2	5 sec
3	>10 minutes[a]

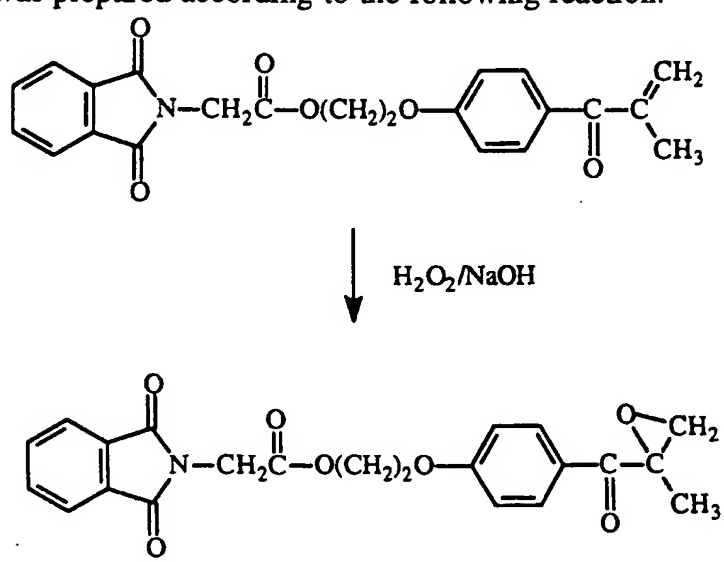
a There is a phase change after 10 minutes due to extreme heat

As shown in Table 4, only composition number 3, the Victoria Pure Blue BO included in cyclodextrin with the radiation transorber covalently attached to the β–cyclodextrin was capable of stabilizing the dye under the mercury discharge light.

Example 12

Preparation of epoxide intermediate of dehydrated phthaloylglycine-2959

The epoxide intermediate of dehydrated phthaloylglycine 2959 was prepared according to the following reaction:



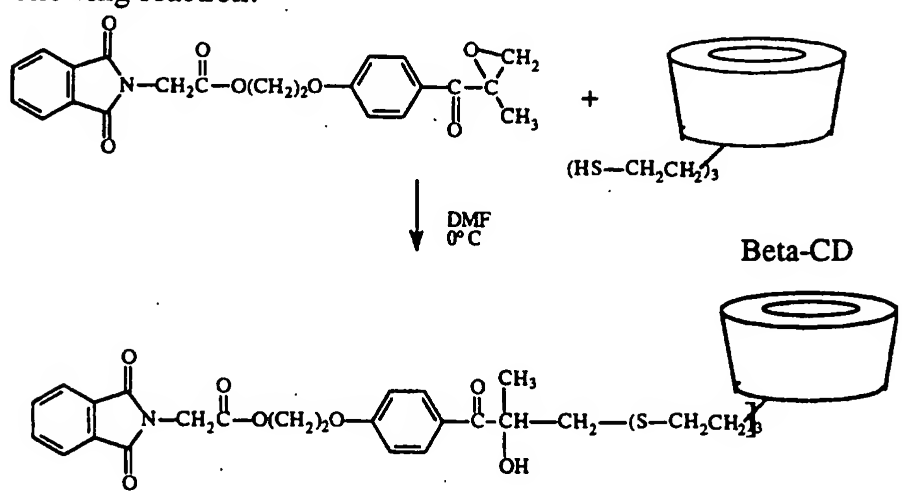
In a 250 ml, three-necked, round bottomed flask fitted with an addition funnel, thermometer and magnetic stirrer was placed 30.0g (0.076 mol) of the dehydrated phthaloylglycine-2959, 70 ml methanol and 20.1 ml hydrogen peroxide (30% solution). The reaction mixture was stirred and cooled in a water/ice bath to maintain a temperature in the range 15°-20° C. 5.8 ml of a 6 N NaOH solution was placed in the addition funnel and the solution was slowly added to maintain the reaction mixture temperature of 15°-20° C. This step took about 4 minutes. The mixture was then stirred for 3 hours at about 20°-25° C. The reaction mixture was then poured into 90 ml of water and extracted with two 70 ml portions of ethyl ether. The organic layers were combined and

washed with 100 ml of water, dried with anhydrous $MgSO_4$, filtered, and the ether removed on a rotary evaporator to yield a white solid (yield 20.3g, 65%). The IR showed the stretching of the C-O-C group and the material was used without further purification.

Example 13

Attachment of epoxide intermediate to thiol cyclodextrin

The attachment of the epoxide intermediate of dehydrated phthaloylglycine 2959 was accomplished according to the following reaction:



In a 250 ml 3-necked round bottomed flask fitted with a stopper and two glass stoppers, all being wired with copper wire and attached to the flask with rubber bands, was placed 30.0 g (0.016 mol) thiol cyclodextrin and 100 ml of anhydrous dimethylformamide (DMF) (Aldrich Chemical Co., Milwaukee, Wisconsin). The reaction mixture was cooled in a ice bath and 0.5 ml diisopropyl ethyl amine was added. Hydrogen sulfide was bubbled into the flask and a positive pressure maintained for 3 hours. During the last hour, the reaction mixture was allowed to warm to room temperature.

The reaction mixture was flushed with argon for 15 minutes and then poured into 70 ml of water to which was then added 100 ml acetone. A white precipitate occurred and was

filtered to yield 20.2 g (84.1%) of a white powder which was used without further purification.

In a 250 ml round bottomed flask fitted with a magnetic stirrer and placed in an ice bath was placed 12.7 (0.031 mol), 80 ml of anhydrous DMF (Aldrich Chemical Co., Milwaukee, Wisconsin) and 15.0 g (0.010 mol) thiol CD. After the reaction mixture was cooled, 0.5 ml of diisopropyl ethyl amine was added and the reaction mixture stirred for 1 hour at 0°C to 5°C followed by 2 hours at room temperature. The reaction mixture was then poured into 200 ml of ice water and a white precipitate formed immediately. This was filtered and washed with acetone. The damp white powder was dried in a convection oven at 80°C for 3 hours to yield a white powder. The yield was 24.5 g (88%).

Example 14

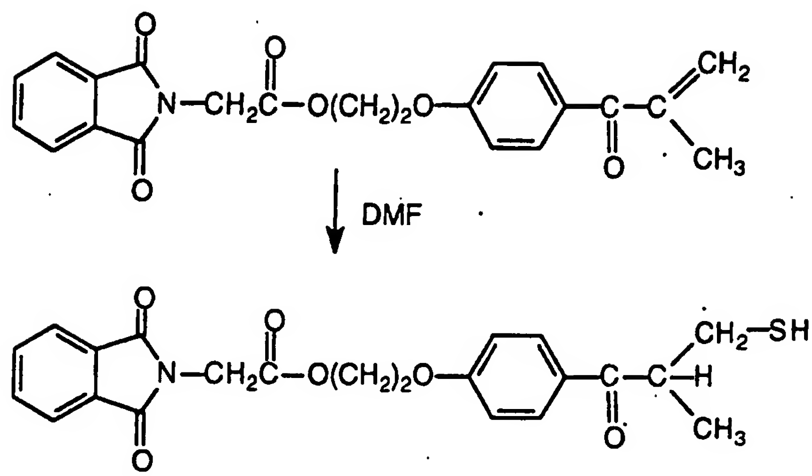
Insertion of Victoria Blue in the cyclodextrin cavity

In a 250 ml Erlenmeyer flask was placed a magnetic stirrer, 40.0 g (0.014 mol) of the compound produced in Example 13 and 100 ml water. The flask was heated on a hot plate to 80°C. When the white cloudy mixture became clear, 7.43 g (0.016 mol) of Victoria Pure Blue BO powder was then added to the hot solution and stirred for 10 minutes then allowed to cool to 50°C. The contents were then filtered and washed with 20 ml of cold water.

The precipitate was then dried in a convention oven at 80°C for 2 hours to yield a blue powder 27.9 g (58.1%).

Example 15

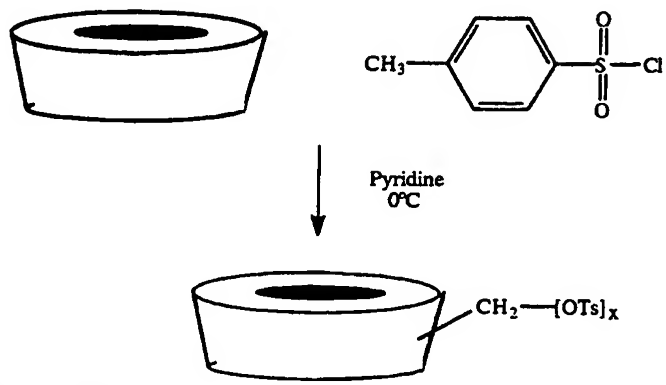
The preparation of a tosylated cyclodextrin with the dehydroxy phthaloylglycine 2959 attached thereto is performed by the following reactions:



To a 500 ml 3-necked round bottomed flask fitted with a bubble tube, condenser and addition funnel, was placed 10 g (0.025 mole) of the dehydrated phthaloylglycine 2959 in 150 ml of anhydrous N,N-diethylformamide (Aldrich Chemical Co., Milwaukee, Wisconsin) cooled to 0°C in an ice bath and stirred with a magnetic stirrer. The synthesis was repeated except that the flask was allowed to warm up to 60°C using a warm water bath and the H_2S pumped into the reaction flask till the stoppers started to move (trying to release the pressure). The flask was then stirred under these conditions for 4 hours. The saturated solution was kept at a positive pressure of H_2S. The stoppers were held down by wiring and rubber bands. The reaction mixture was then allowed to warm-up overnight. The solution was then flushed with argon for 30 minutes and the reaction mixture poured onto 50 g of crushed ice and extracted three times (3 x 80 ml) with diethyl ether (Aldrich Chemical Co., Milwaukee, Wisconsin).

The organic layers were condensed and washed with water and dried with $MgSO_4$. Removal of the solvent on a rotary evaporator gave 5.2 g of a crude product. The product was purified on a silica column using 20% ethyl acetate in hexane as eluant. 4.5 g of a white solid was obtained.

A tosylated cyclodextrin was prepared according to the following reaction:



To a 100 ml round bottomed flask was placed 6.0 g ß-cyclodextrin (American Maize Product Company), 10.0g (0.05 mole) *p*-toluenesulfonyl chloride (Aldrich Chemical Co., Milwaukee, Wisconsin), 50 ml of pH 10 buffer solution (Fisher). The resultant mixture was stirred at room temperature for 8 hours after which it was poured on ice (approximately 100 g) and extracted with diethyl ether. The aqueous layer was then poured into 50 ml of acetone (Fisher) and the resultant, cloudy mixture filtered. The resultant white powder was then run through a sephadex column (Aldrich Chemical Co., Milwaukee, Wisconsin) using n-butanol, ethanol, and water (5:4:3 by volume) as eluant to yield a white powder. The yield was 10.9%.

The degree of substitution of the white powder (tosyl-cyclodextrin) was determined by ^{13}C NMR spectroscopy (DMF-d6) by comparing the ratio of hydroxysubstituted carbons versus tosylated carbons, both at the 6 position. When the 6-position carbon bears a hydroxy group, the NMR peaks for each of the six carbon atoms are given in Table 5.

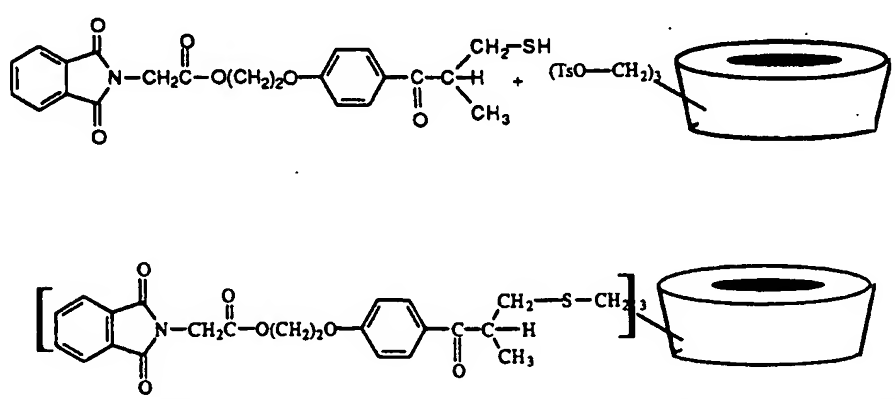
Table 5

Carbon Atom	NMR Peak (ppm)
1	101.8
2	72.9
3	72.3
4	81.4
5	71.9
6	59.8

The presence of the tosyl group shifts the NMR peaks of the 5-position and 6-position carbon atoms to 68.8 and 69.5 ppm, respectively.

The degree of substitution was calculated by integrating the NMR peak for the 6-position tosylated carbon, integrating the NMR peak for the 6-position hydroxy-substituted carbon, and dividing the former by the latter. The integrations yielded 23.6 and 4.1, respectively, and a degree of substitution of 5.9. Thus, the average degree of substitution in this example is about 6.

The tosylated cyclodextrin with the dehydroxy phthaloylglycine 2959 attached was prepared according to the following reaction:



To a 250 ml round bottomed flask was added 10.0 g (4-8 mole) of tosylated substituted cyclodextrin, 20.7g (48 mmol) of thiol (mercapto dehydrated phthaloylglycine 2959) in 100 ml of DMF. The reaction mixture was cooled to 0° C in an ice bath and

stirred using a magnetic stirrer. To the solution was slowly dropped in 10 ml of ethyl diisopropylamine (Aldrich Chemical Co., Milwaukee, Wisconsin) in 20 ml of DMF. The reaction was kept at 0° C for 8 hours with stirring. The reaction mixture was extracted with diethyl ether. The aqueous layer was then treated with 500 ml of acetone and the precipitate filtered and washed with acetone. The product was then run on a sephadex column using n-butanol, ethanol, and water (5:4:3 by volume) to yield a white powder. The yield was 16.7 g.

The degree of substitution of the functionalized molecular includant was determined as described above. In this case, the presence of the derivatized ultraviolet radiation transorber shifts the NMR peak of the 6-position carbon atom to 63.1. The degree of substitution was calculated by integrating the NMR peak for the 6-position substituted carbon, integrating the NMR peak for the 6-position hydroxy-substituted carbon, and dividing the former by the latter. The integrations yielded 67.4 and 11.7, respectively, and a degree of substitution of 5.7. Thus, the average degree of substitution in this example is about 6. The reaction above shows the degree of substitution to be "n". Although n represents the value of substitution on a single cyclodextrin, and therefore, can be from 0 to 24, it is to be understood that the average degree of substitution is about 6.

Example 16

The procedure of Example 15 was repeated, except that the amounts of β-cyclodextrin and *p*-toluenesulfonic acid (Aldrich) were 6.0 g and 5.0 g, respectively. In this case, the degree of substitution of the cyclodextrin was found to be about 3.

Example 17

The procedure of Example 15 was repeated, except that the derivatized molecular includant of Example 16 was employed in place of that from Example 15. The average degree of

substitution of the functionalized molecular includant was found to be about 3.

Example 18

This example describes the preparation of a colored composition which includes a mutable colorant and the functionalized molecular includant from Example 15.

In a 250-ml Erlenmeyer flask containing a magnetic stirring bar was placed 20.0 g (5.4 mmoles) of the functionalized molecular includant obtained in Example 15 and 100 g of water. The water was heated to 80°C, at which temperature a clear solution was obtained. To the solution was added slowly, with stirring, 3.1 g (6.0 mmoles) of Victoria Pure Blue BO (Aldrich). A precipitate formed which was removed from the hot solution by filtration. The precipitate was washed with 50 ml of water and dried to give 19.1 g (84 percent) of a blue powder, a colored composition consisting of a mutable colorant, Victoria Pure Blue B0, and a molecular includant having covalently coupled to it an average of about six ultraviolet radiation transorber molecules per molecular includant molecule.

Example 19

The procedure of Example 18 was repeated, except that the functionalized molecular includant from Example 17 was employed in place of that from Example 15.

Example 20

This example describes mutation or decolorization rates for the compositions of Examples 7 (wherein the beta-cyclodextrin has dehydrated phthaloyl glycine-2959 from Example 4 covalently bonded thereto), 18 and 19.

In each case, approximately 10 mg of the composition was placed on a steel plate (Q-Panel Company, Cleveland, Ohio). Three drops (about 0.3 ml) of acetonitrile (Burdick & Jackson, Muskegon, Michigan) was placed on top of the composition and

the two materials were quickly mixed with a spatula and spread out on the plate as a thin film. Within 5-10 seconds of the addition of the acetonitrile, each plate was exposed to the radiation from a 222-nanometer excimer lamp assembly. The assembly consisted of a bank of four cylindrical lamps having a length of about 30 cm. The lamps were cooled by circulating water through a centrally located or inner tube of the lamp and, as a consequence, they operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically was in the range of from about 4 to about 20 joules per square meter (J/m^2). However, such range in reality merely reflects the capabilities of current excimer lamp power supplies; in the future, higher power densities may be practical. The distance from the lamp to the sample being irradiated was 4.5 cm. The time for each film to become colorless to the eye was measured. The results are summarized in Table 6.

Table 6

Decolorization Times for Various Compositions

Composition	Decolorization Times (Seconds)
Example 18	1
Example 19	3-4
Example 7	7-8

While the data in Table 6 demonstrate the clear superiority of the colored compositions of the present invention, such data were plotted as degree of substitution versus decolorization time. The plot is shown in Figure 3. Figure 3 not only demonstrates the significant improvement of the colored compositions of the present invention when compared with compositions having a degree of substitution less than three, but also indicates that a degree of substitution of about 6 is about optimum. That is, the figure indicates that little if any improvement in decolonization

time would be achieved with degrees of substitution greater than about 6.

Example 21

This example describes the preparation of a complex consisting of a mutable colorant and the derivatized molecular includant of Example 15.

The procedure of Example 18 was repeated, except that the functionalized molecular includant of Example 15 was replaced with 10 g (4.8 mmoles) of the derivatized molecular includant of Example 15 and the amount of Victoria Pure Blue BO was reduced to 2.5 g (4.8 mmoles). The yield of washed solid was 10.8 g (86 percent) of a mutable colorant associated with the β-cyclodextrin having an average of six tosyl groups per molecule of molecular includant.

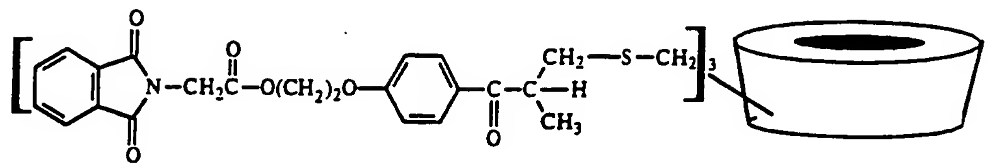
Example 22

This example describes the preparation of a colored composition which includes a mutable colorant and a functionalized molecular includant.

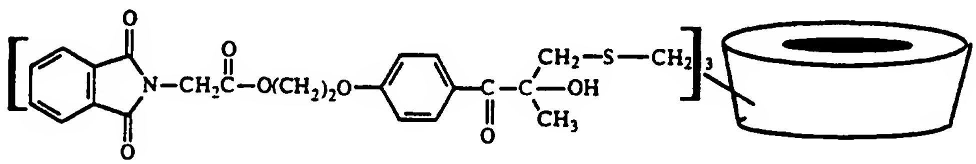
The procedure of preparing a functionalized molecular includant of Example 15 was repeated, except that the tosylated B-cyclodextrin was replaced with 10 g (3.8 mmoles) of the complex obtained in Example 21 and the amount of the derivatized ultraviolet radiation transorber prepared in Example 15 was 11.6 g (27 mmoles). The amount of colored composition obtained was 11.2 g (56 percent). The average degree of substitution was determined as described above, and was found to be 5.9, or about 6.

Example 23

The two compounds represented by the following formulas were tested for their ability to stabilize Victoria Pure Blue BO:



Dehydroxy Compound



Hydroxy Compound

This example further demonstrates the ability of the present invention to stabilize colorants against light. The two compounds containing Victoria Pure Blue BO as an includant in the cyclodextrin cavity were tested for light fastness under a medium pressure mercury discharge lamp. 100 mg of each compound was dissolved in 20 ml of acetonitrile and was uniformly spread on steel plates to a thickness of approximately 0.1 mm. The plates were then immediately exposed to a medium pressure 1200 watt high intensity quartz arc mercury discharge lamp (Conrad-Hanovia, Inc., Newark, New Jersey) at a distance of 30 cm from the lamp. The light fastness results of these compounds are summarized in Table 7.

Table 7

Cyclodextrin Compound	Fade Time
Dehydroxy Compound	>10 min[a]
Hydroxy Compound	<20 sec

a There is a phase change after 10 minutes due to extreme heat

Example 24

This example describes the preparation of films consisting of colorant, ultraviolet radiation transorber, and thermoplastic polymer. The colorant and ultraviolet radiation transorber were ground separately in a mortar. The desired amounts of the ground components were weighed and placed in an aluminum pan, along with a weighed amount of a thermoplastic polymer. The pan was placed on a hot plate set at 150°C and the mixture in the pan was stirred until molten. A few drops of the molten mixture were poured onto a steel plate and spread into a thin film by means of a glass microscope slide. Each steel plate was 3 x 5 inches (7.6 cm x 12.7 cm) and was obtained from Q-Panel Company, Cleveland, Ohio. The film on the steel plate was estimated to have a thickness of the order of 10-20 micrometers.

In every instance, the colorant was Malachite Green oxalate (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), referred to hereinafter as Colorant A for convenience. The ultraviolet radiation transorber ("UVRT") consisted of one or more of Irgacure® 500 ("UVRT A"), Irgacure® 651 ("UVRT B"), and Irgacure® 907 ("UVRT C"), each of which was described earlier and is available from Ciba-Geigy Corporation, Hawthorne, New York. The polymer was one of the following: an epichlorohydrin-bisphenol A epoxy resin ("Polymer A"), Epon® 1004F (Shell Oil Company, Houston, Texas); a poly(ethylene glycol) having a weight-average molecular weight of about 8,000 ("Polymer B"), Carbowax 8000 (Aldrich Chemical Company); and a poly(ethylene glycol) having a weight-average molecular weight of about 4,600 ("Polymer C"), Carbowax 4600 (Aldrich Chemical Company). A control film was prepared which consisted only of colorant and polymer. The compositions of the films are summarized in Table 8.

Table 8
Compositions of Films Containing
Colorant and Ultraviolet Radiation Transorber ("UVRT")

	Colorant		UVRT		Polymer	
Film	Type	Parts	Type	Parts	Type	Parts
A	A	1	A	6	A	90
			C	4		
B	A	1	A	12	A	90
			C	8		
C	A	1	A	18	A	90
			C	12		
D	A	1	A	6	A	90
			B	4		
E	A	1	B	30	A	70
F	A	1	--	--	A	100
G	A	1	A	6	B	90
			C	4		
H	A	1	B	10	C	90

While still on the steel plate, each film was exposed to ultraviolet radiation. In each case, the steel plate having the film sample on its surface was placed on a moving conveyor belt having a variable speed control. Three different ultraviolet radiation sources, or lamps, were used. Lamp A was a 222-nanometer excimer lamp and Lamp B was a 308-nanometer excimer lamp, as already described. Lamp C was a fusion lamp system having a "D" bulb (Fusion Systems Corporation, Rockville, Maryland). The excimer lamps were organized in banks of four cylindrical lamps having a length of about 30 cm, with the lamps being oriented normal to the direction of motion of the belt. The lamps were cooled by circulating water through a centrally located or inner tube of the lamp and, as a consequence, they operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface

typically is in the range of from about 4 to about 20 joules per square meter (J/m^2).

However, such range in reality merely reflects the capabilities of current excimer lamp power supplies; in the future, higher power densities may be practical. With Lamps A and B, the distance from the lamp to the film sample was 4.5 cm and the belt was set to move at 20 ft/min (0.1 m/sec). With Lamp C, the belt speed was 14 ft/min (0.07 m/sec) and the lamp-to-sample distance was 10 cm. The results of exposing the film samples to ultraviolet radiation are summarized in Table 9. Except for Film F, the table records the number of passes under a lamp which were required in order to render the film colorless. For Film F, the table records the number of passes tried, with the film in each case remaining colored (no change).

Table 9

Results of Exposing Films Containing Colorant and Ultraviolet Radiation Transorber (UVRT) to Ultraviolet Radiation

	Excimer Lamp		
Film	**Lamp A**	**Lamp B**	**Fusion Lamp**
A	3	3	15
B	2	3	10
C	1	3	10
D	1	1	10
E	1	1	1
F	5	5	10
G	3	--	10
H	3	--	10

Example 25

This Example demonstrates that the 222 nanometer excimer lamps illustrated in Figure 4 produce uniform intensity readings on a surface of a substrate 5.5 centimeters from the lamps, at the numbered locations, in an amount sufficient to mutate the colorant

in the compositions of the present invention which are present on the surface of the substrate. The lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m^2).

Table 10 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate. The readings numbered 1, 4, 7, and 10 were located approximately 7.0 centimeters from the left end of the column as shown in Figure 4. The readings numbered 3, 6, 9, and 12 were located approximately 5.5 centimeters from the right end of the column as shown in Figure 4. The readings numbered 2, 5, 8, and 11 were centrally located approximately 17.5 centimeters from each end of the column as shown in Figure 4.

TABLE 10

Background (μW)	Reading (mW/cm^2)
24.57	9.63
19.56	9.35
22.67	9.39
19.62	9.33
17.90	9.30
19.60	9.30
21.41	9.32
17.91	9.30
23.49	9.30
19.15	9.36
17.12	9.35
21.44	9.37

Example 26

This Example demonstrates that the 222 nanometer excimer lamps illustrated in Figure 5 produce uniform intensity readings on a surface of a substrate 5.5 centimeters from the lamps, at the numbered locations, in an amount sufficient to mutate the colorant in the compositions of the present invention which are present on the surface of the substrate. The excimer lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m^2).

Table 11 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate. The readings numbered 1, 4, and 7 were located approximately 7.0 centimeters from the left end of the columns as shown in Figure 5. The readings numbered 3, 6, and 9 were located approximately 5.5 centimeters from the right end of the columns as shown in Figure 5. The readings numbered 2, 5, 8 were centrally located approximately 17.5 centimeters from each end of the columns as shown in Figure 5.

Table 11

Background (μW)	Reading (mW/cm^2)
23.46	9.32
16.12	9.31
17.39	9.32
20.19	9.31
16.45	9.29
20.42	9.31
18.33	9.32
15.50	9.30
20.90	9.34

Example 27

This Example demonstrates the intensity produced by the 222 nanometer excimer lamps illustrated in Figure 6, on a surface of a substrate, as a function of the distance of the surface from the lamps, the intensity being sufficient to mutate the colorant in the compositions of the present invention which are present on the surface of the substrate. The excimer lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m^2).

Table 12 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate at position 1 as shown in Figure 6. Position 1 was centrally located approximately 17 centimeters from each end of the column as shown in Figure 6.

Table 12

Distance (cm)	Background (μW)	Reading (mW/cm^2)
5.5	18.85	9.30
6.0	15.78	9.32
10	18.60	9.32
15	20.90	9.38
20	21.67	9.48
25	19.86	9.69
30	22.50	11.14
35	26.28	9.10
40	24.71	7.58
50	26.95	5.20

Having thus described the invention, numerous changes and modifications hereof will be readily apparent to those having ordinary skill in the art, without departing from the spirit or scope of the invention.

CLAIMS

What is claimed is:

1. A recording medium comprising a substrate and a recording layer disposed thereon, the recording layer comprising a colored composition comprising a colorant and a radiation transorber, the colorant being mutable upon exposure of the composition to ultraviolet radiation, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator.

2. The recording medium of Claim 1, wherein the substrate is a disk.

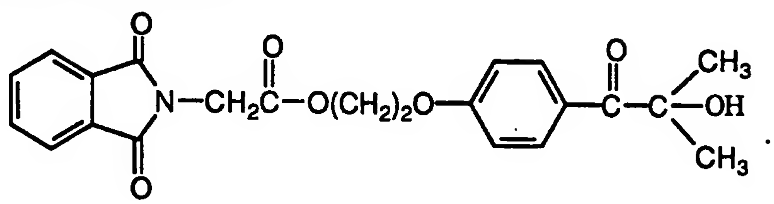
3. The recording medium of Claim 1, wherein the recording layer further comprises a molecular includant.

4. The recording medium of Claim 3, wherein the colorant and radiation transorber are associated with the molecular includant.

5. The recording medium of Claim 3, wherein the molecular includant is a clathrate or intercalate.

6. The recording medium of Claim 3, wherein the molecular includant is a zeolite or cyclodextrin.

7. The recording medium of Claim 1, wherein the radiation transorber is



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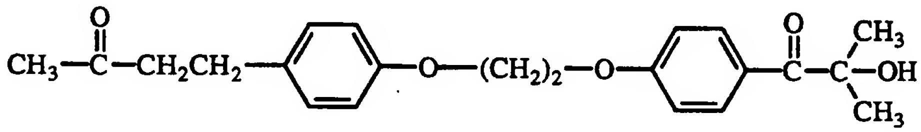


8. A recording medium comprising a substrate and a colored composition contained therein, the colored composition comprising a colorant and a radiation transorber, the colorant being mutable upon exposure of the composition to ultraviolet radiation, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator.

9. The recording medium of Claim 8, wherein the substrate is a disk.

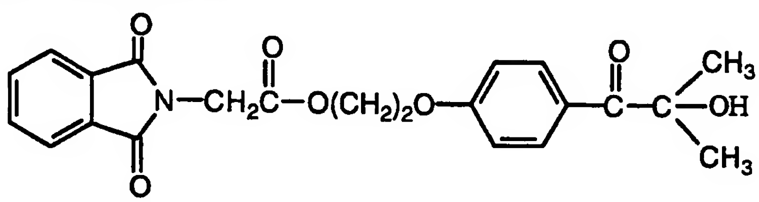
10. The recording medium of Claim 8, wherein the colored composition further comprises a molecular includant.

11. The recording medium of Claim 10, wherein the colorant and radiation transorber are associated with the molecular includant.

12. The recording medium of Claim 10, wherein the molecular includant is a clathrate or intercalate.

13. The recording medium of Claim 10, wherein the molecular includant is a zeolite or cyclodextrin.

14. The recording medium of Claim 8, wherein the radiation transorber is



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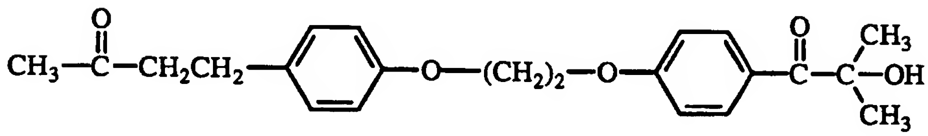


15. A method of recording information onto a recording medium comprising, selectively irradiating portions of a layer of a colored composition comprising a colorant and a radiation transorber with sufficient ultraviolet radiation to mutate the color of the colorant at the irradiated portions, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator.

16. The method of Claim 15, wherein the layer is formed on a substrate.

17. The method of Claim 16, wherein the substrate is a disk.

18. The method of Claim 15, wherein the layer is formed in a substrate.

19. The method of Claim 18, wherein the substrate is a disk.

20. The method of Claim 15, wherein the colored composition further comprises a molecular includant.

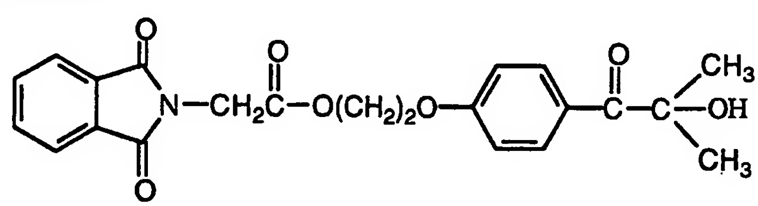
21. The method of Claim 20, wherein the substrate is a disk.

22. The method of Claim 20, wherein the colorant and radiation transorber are associated with the molecular includant.

23. The method of Claim 20, wherein the molecular includant is a clathrate or intercalate.

24. The method of Claim 20, wherein the molecular includant is a zeolite or cyclodextrin.

25. The method of Claim 15, wherein the radiation transorber is



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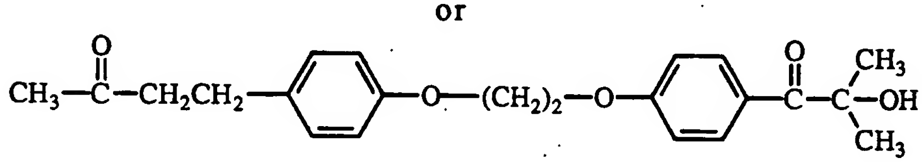


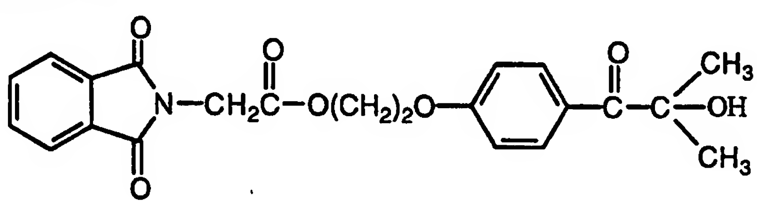
26. A method of reading information from a recording medium comprising a layer of a colored composition comprising a colorant and a radiation transorber, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, the method comprising:

sequentially illuminating portions of the layer with non-mutating radiation; and

detecting the radiation reflected by the illuminated portions, the colorant being substantially color-stable upon exposure of the composition to sunlight and artificial light.

27. The method of Claim 26, wherein the colored composition further comprises a molecular includant.

28. The method of Claim 26, wherein the radiation transorber is



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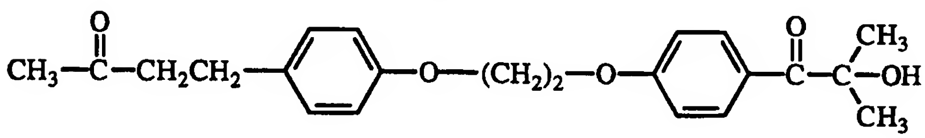
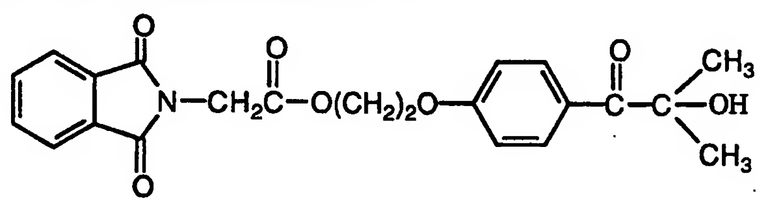


29. An optically recordable disk comprising a disk body having a recording layer formed therewith, the recording layer comprising a mutable colored composition comprising a colorant and an ultraviolet radiation transorber, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, selected portions of the colored composition being mutable upon exposure to mutating radiation while adjacent portions which are not exposed to mutating radiation are not mutated, the mutated and non-mutated portions having different light reflectivities.

30. The optically recordable disk of Claim 29, wherein the mutable colored composition further comprises a molecular includant.

31. The optically recordable disk of Claim 29, wherein the radiation transorber is



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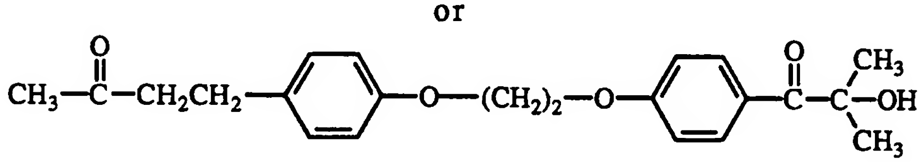
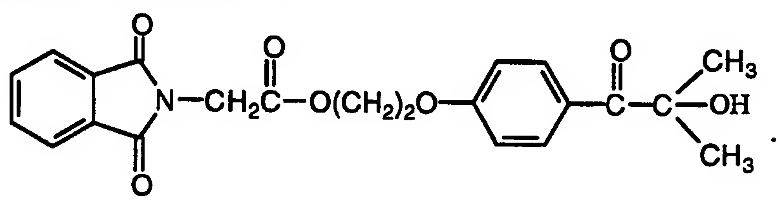


32. An optically readable disk comprising a disk body having a recording layer formed therewith, the recording layer comprising a mutable colored composition comprising a colorant and a radiation transorber, the radiation transorber comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, the recording layer comprising regions where the colorant has been mutated and regions where the colorant has not been mutated, the mutated and non-mutated portions having different light reflectivities, the regions of mutated and non-mutated colorant representing digitally encoded signals.

33. The optically readable disk of Claim 32, wherein the colored composition further comprises a molecular includant.

34. The optically readable disk of Claim 32, wherein the radiation transorber is



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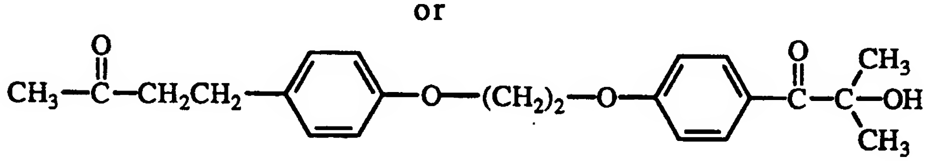


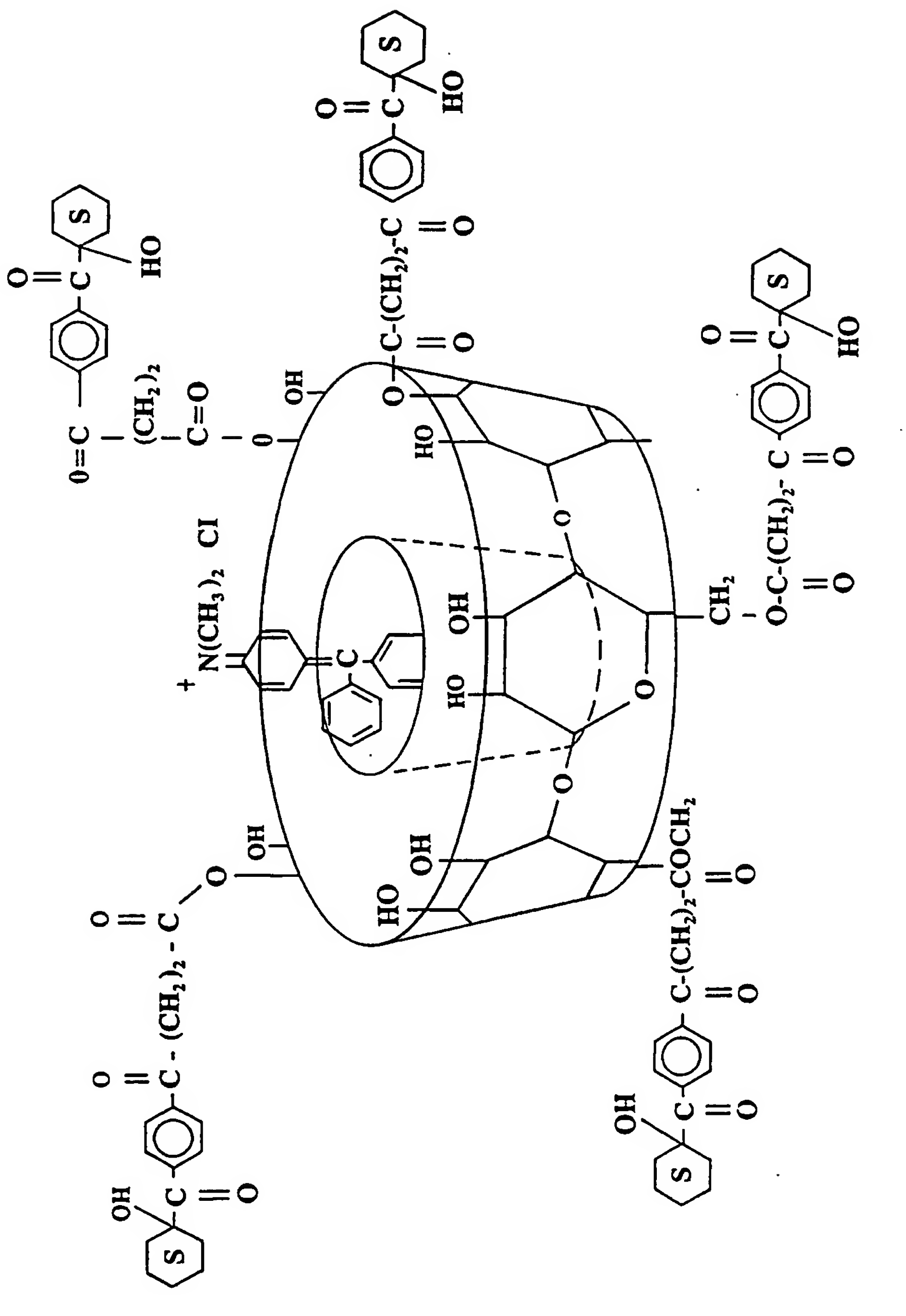


Fig. 1

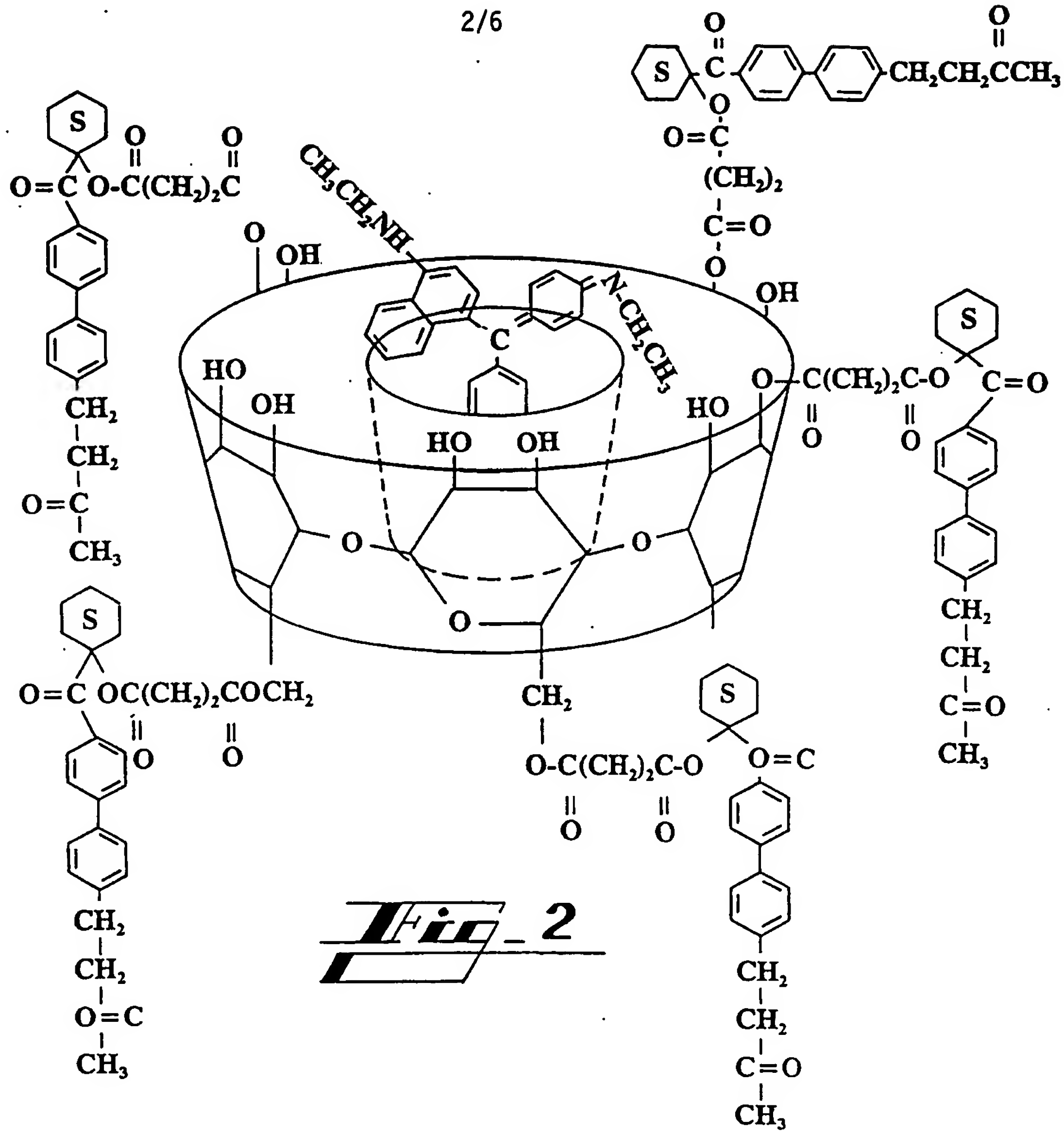


Fig_2

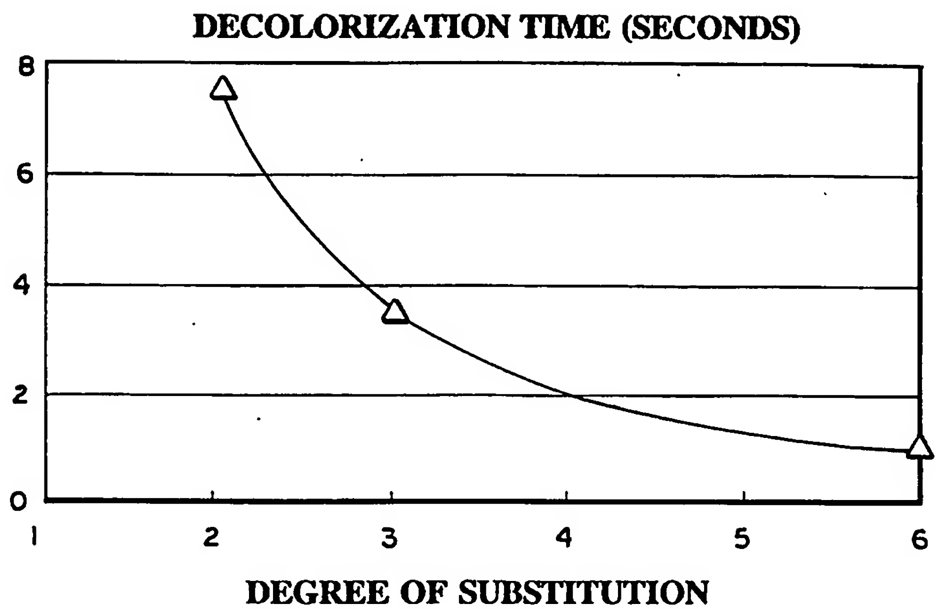

DECOLORIZATION TIME (SECONDS)
8
6
4
2
0
1
2
3
4
5
6
DEGREE OF SUBSTITUTION

Fig_3

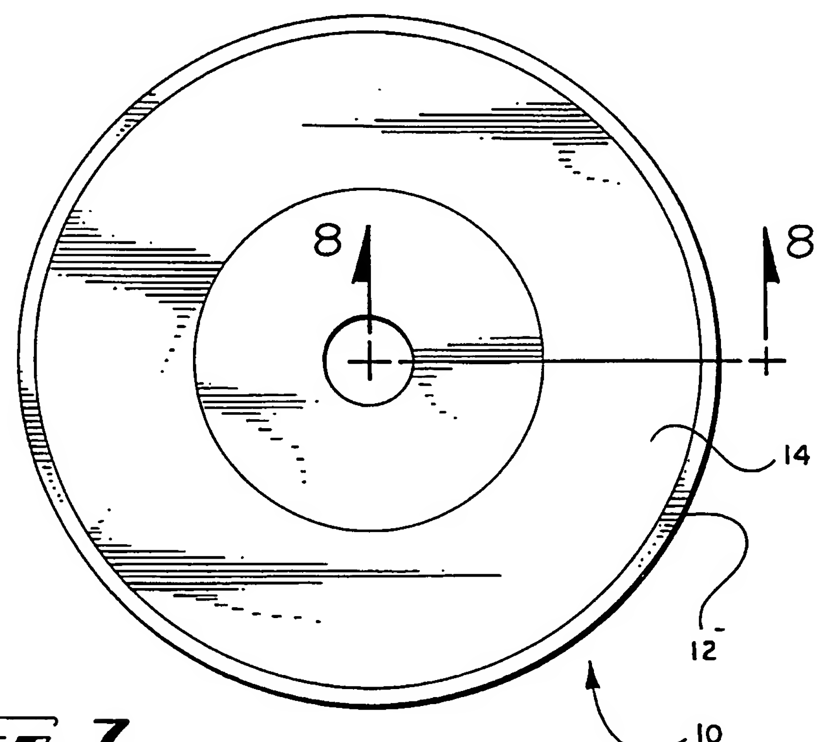

8
8
14
12
10

Fig_7

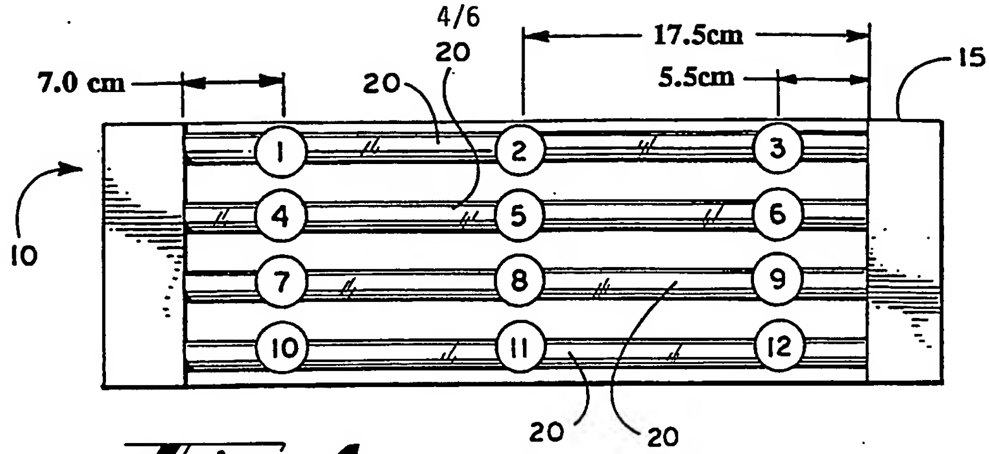


Fig. 4

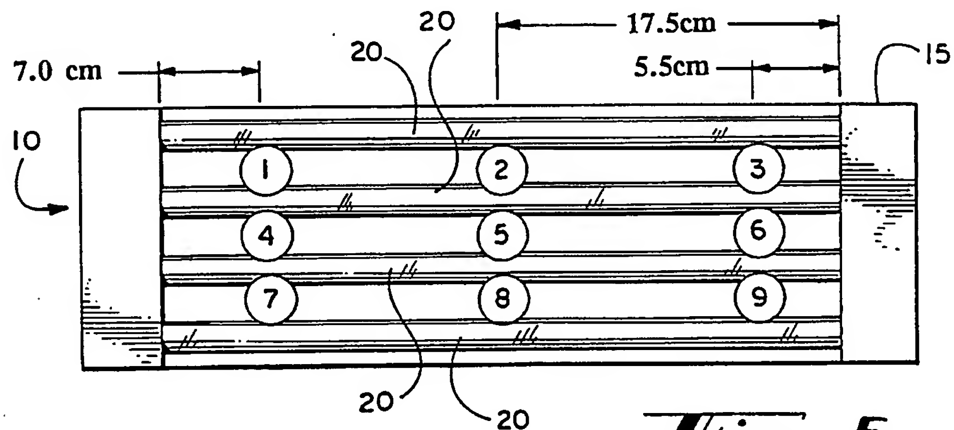
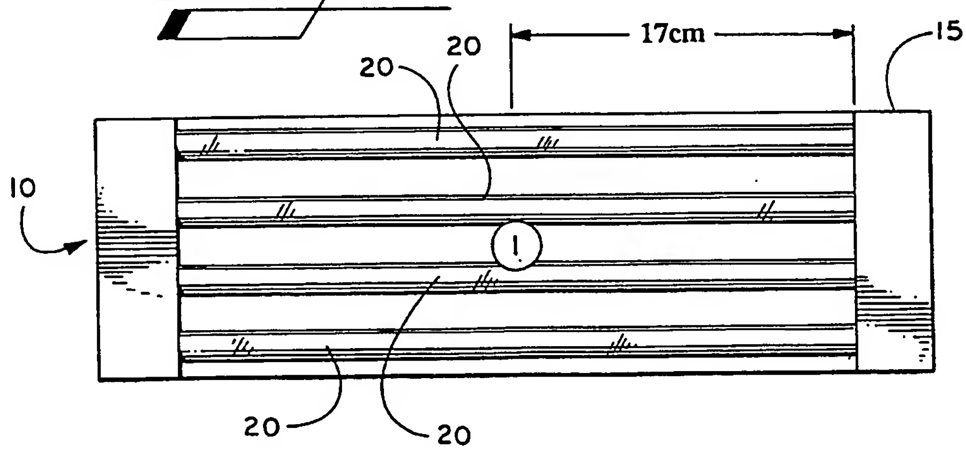


Fig. 5

Fig. 6



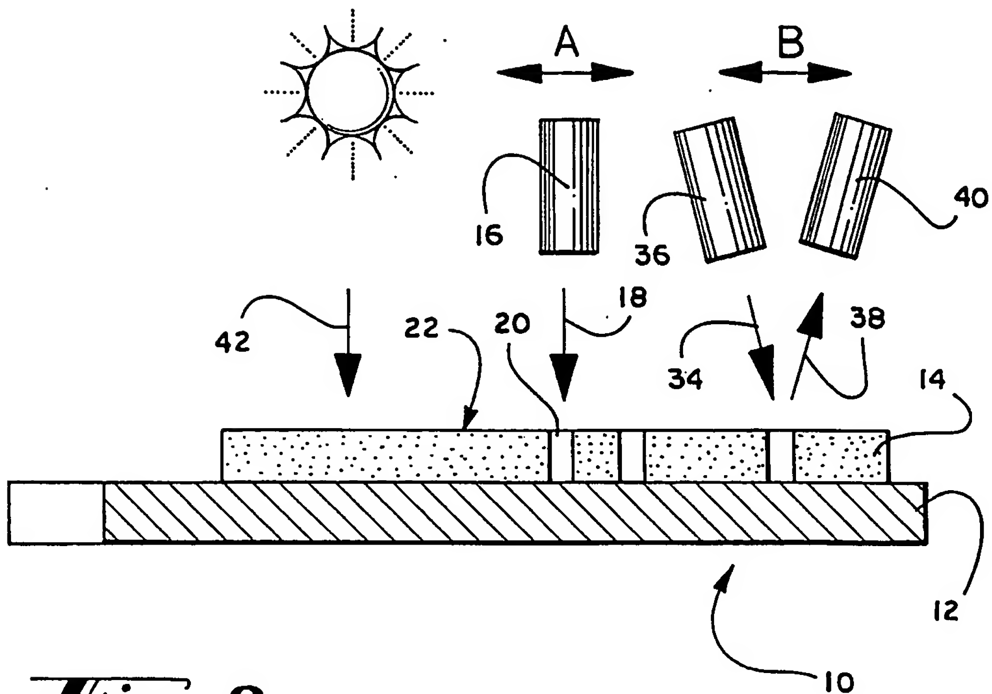

A
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Fig_8

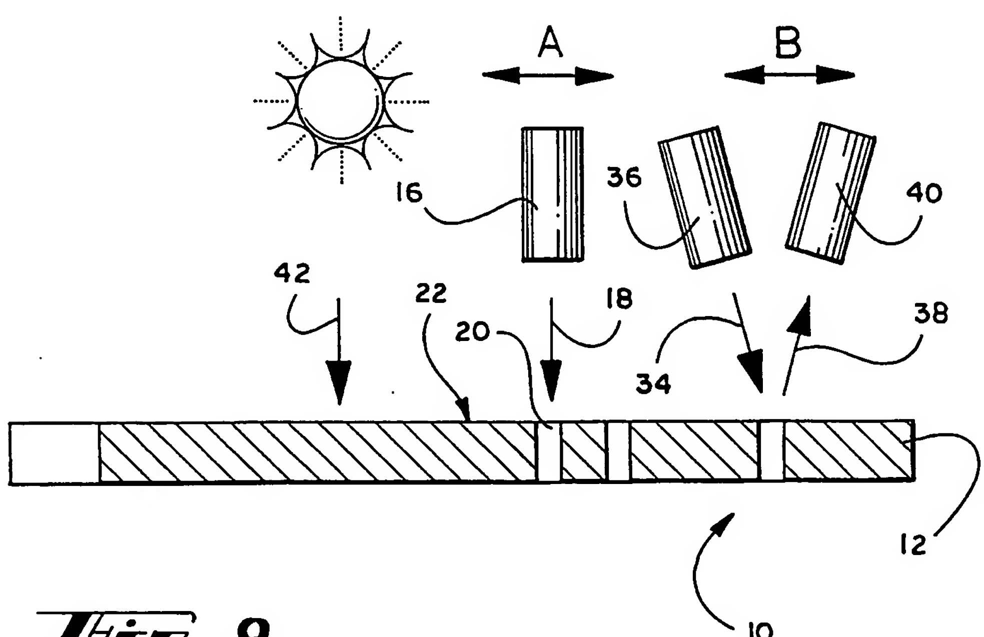
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Fig_9

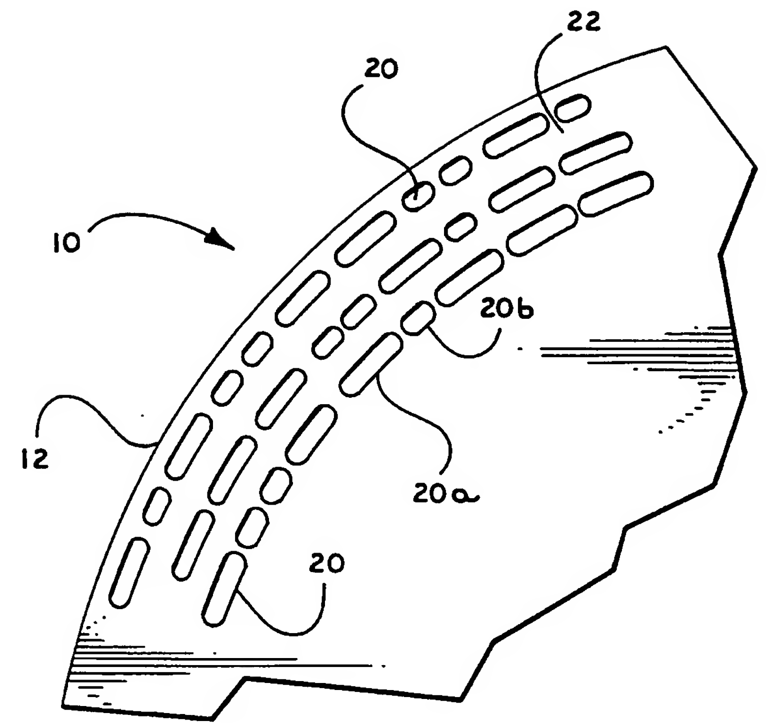

Fig_10

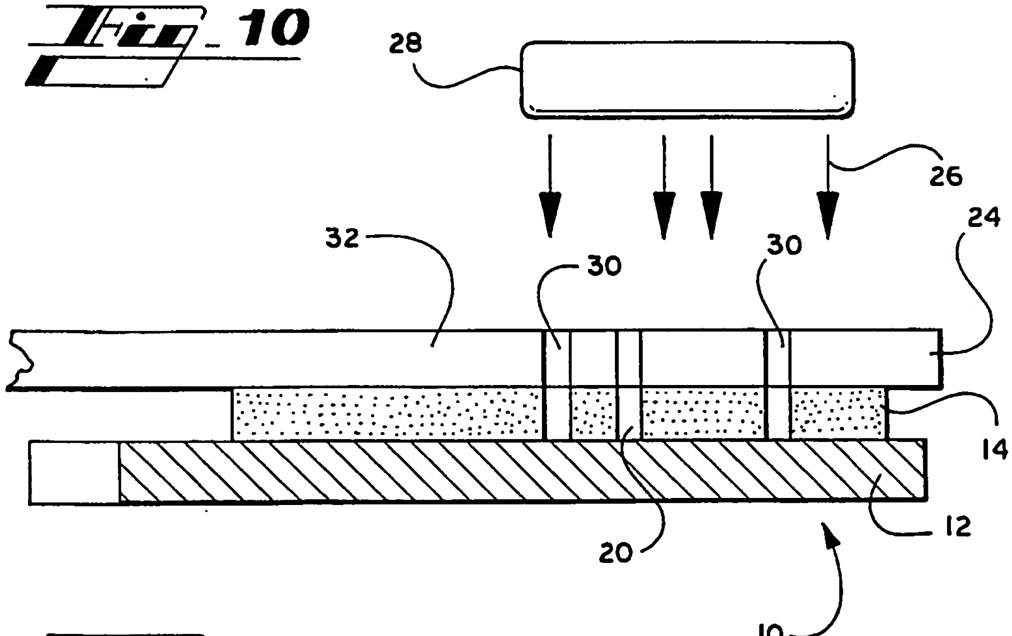

Fig_11

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/08445

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,95 04955 (KIMBERLY-CLARK CORPORATION) 16 February 1995 see the whole document -----	1-25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 1996	27.09.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Heywood, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 96/08445

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9504955	16-02-95	AU-A-	7517394	28-02-95
		CA-A-	2120838	06-02-95
		CA-A-	2168727	16-02-95
		EP-A-	0712506	22-05-96
		FI-A-	960483	06-03-96
		NO-A-	960455	02-04-96
		PL-A-	312835	13-05-96
		CA-A-	2123281	11-03-95